

Unified Description of Thermal and Nonthermal Hot Carriers in Plasmonic Photocatalysis

Published as part of *The Journal of Physical Chemistry C* special issue “Naomi Halas and Peter Nordlander Festschrift”.

Yu Chen, Shengxiang Wu, and Shiwu Gao*



Cite This: *J. Phys. Chem. C* 2025, 129, 12804–12813



Read Online

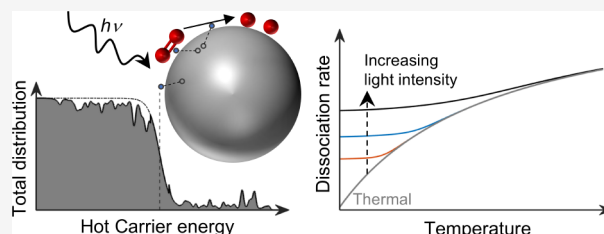
ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The damping of surface plasmons generates hot carriers, which hold promise for photoelectric conversion and photocatalysis. Recent studies have revealed the nonequilibrium characters of the plasmonic hot carriers and their nonadiabatic coupling to molecular vibrations. However, the precise mechanism of plasmonic photocatalysis remains elusive and controversial. Here, we present a unified description of thermal and nonthermal hot carriers in the dynamics of vibrational excitation and photodissociation, in which a quantitative comparison between the two mechanisms can be made.

We revisit a well-studied system, O_2 dissociation on silver nanoparticles. The nonthermal hot carriers are found to promote molecular dissociation in the low-temperature or high-intensity regime. With increasing laser intensity, the dissociation rate exhibits a transition from a linear to nonlinear dependence, due to the onset of vibrational heating, as observed in experiments. Our model provides a unified framework to understand the mechanism and dynamics of photocatalysis and reveals the nonthermal pathways for energy harvesting and conversion with surface plasmons.



INTRODUCTION

Since the pioneering works of plasmon-induced dissociation of O_2/H_2 on noble metal nanoparticles,^{1–4} plasmonic photochemistry has evolved into an active research field with promising energy applications.^{5–29} The hot carriers generated by Landau damping of surface plasmons have been suggested to be the dominant mechanism,^{1–18} due to the efficient injection and separation of plasmonic hot carriers across the interface.^{30–39} Such an electronic mechanism is common in electron- and photochemistry on solid surfaces, which is inevitably competed by possible thermal heating at ambient conditions and under irradiations.^{21,22,40,41} This competition can be more complicated at the plasmonic hot spots of nanoparticle aggregates, where local heating^{42,43} is hard to measure experimentally.^{21,41} Recently, progresses have been made to disentangle the effects of hot carriers from photothermal heating using improved control measurements of surface temperatures,^{44–49} yet the debate between thermal and nonthermal mechanisms remains inconclusive.

Theoretical studies of plasmon-induced hot carrier generation based on electron gas models^{50–54} or atomistic simulations^{55–65} have shown highly nonthermal characters in the energy distributions. Whether and how these nonthermal hot carriers participate directly in surface photochemistry remain challenging for first-principles time-dependent density functional theory (TDDFT) simulations.^{24–27} Phenomeno-

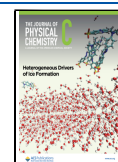
logical descriptions of molecular dissociation have been based exclusively on Arrhenius laws with modified energy barriers and/or local temperatures,^{10–12,21,22} which literally assume quasi-equilibrium distributions achieved in the electronic and/or vibrational degrees of freedom. Such an assumption contradicts with more recent experiments and TDDFT calculations, which show: (1) highly nonthermal characters of hot carrier injection and separation at the metal–semiconductor interface in first-principles simulations,^{36,37,39} (2) ultrafast time scale of charge transfer in comparison with the much longer thermalization time within the nanoparticles,^{32–35} (3) nonthermal hot carrier distributions in direct optical measurements,^{66–70} and (4) nonthermal vibrational populations^{71,72} and mode-specific vibrational temperatures of adsorbed molecules.^{18,73–75} All of these observations demonstrate the nonequilibrium nature of the plasmonic hot carriers and the induced vibrational excitations, which remain to be understood.

Received: December 10, 2024

Revised: May 27, 2025

Accepted: June 26, 2025

Published: July 9, 2025



The Anderson–Newns Hamiltonian^{76,77} with a linear electron-vibration coupling to truncated harmonic oscillators has been appealing to effectively account for the dynamical activation of molecular vibrations by plasmonic hot carriers,^{71,72,78–80} treating bond breaking in the DIET (desorption induced by electronic transition^{81,82}) and/or DIMET (desorption induced by multiple electronic transitions⁸³) mechanisms. For example, Linic and co-workers have adopted this model to explain their experimental findings,^{1,2} including the light intensity dependence and the kinetic isotope effect. Unfortunately, the invoked formulation⁸⁴ considered only a single inelastic scattering event with fixed carrier energy at the molecular resonance and literally omitted all possible contributions from hot carriers in a wide energy spectrum with nonthermal distributions, which have been identified by numerous TDDFT simulations^{36,37,64,65} and the latest experimental measurements.^{66–70} As a result, the effects of nonthermal hot carriers on photocatalysis, and their possible competition with thermal carriers and the photothermal heating mechanism,^{12,21,22,41,44–49} remain unresolved.

We have recently developed a unified description of vibrational excitation induced by both thermal and nonthermal hot carriers,²³ where an explicit form of the nonthermal distribution of plasmonic hot carriers has been introduced. It allows for a quantitative comparison between nonthermal and thermal excitation mechanisms. This paper presents a comprehensive description of the model and important extensions to separate the electron and hole channels of nonthermal excitations, and to incorporate vibrational heating in a wide range of temperatures and light intensities. The mode-specific electron-vibration coupling provides direct physical insight into the mode-dependent vibrational excitations observed in recent experiments.^{18,71–75} As an application of this model, we reanalyzed O₂ dissociation on silver nanoparticle (AgNP) as functions of light intensities and temperatures. We found that beyond a moderate light intensity, local vibrational heating through multiple electronic scatterings outweighed the DIET mechanism for plasmonic photocatalysis. This reproduced the nonlinear dissociation rates at higher light intensities.^{2,3,9–11} Our work provides a unified framework to understand hot carrier photochemistry starting from optical absorption and electron-vibration coupling and bridges the gap between the thermal and nonthermal mechanisms for plasmonic photocatalysis.

METHODS

Hamiltonian. The nanoparticle–molecule system is described by the Anderson–Newns model^{76,77} with a linear electron-vibration coupling to a truncated harmonic oscillator.^{84–90} The total Hamiltonian is comprised of the following three parts:

$$H = H_e + H_v + H_i \quad (1)$$

where

$$H_e = \varepsilon_a c_a^\dagger c_a + \sum_k \varepsilon_k c_k^\dagger c_k + \sum_k (v_{ak} c_a^\dagger c_k + \text{H. c.}) \quad (2a)$$

$$H_v = \hbar\Omega b^\dagger b \quad (2b)$$

$$H_i = \lambda c_a^\dagger c_a (b^\dagger + b) \quad (2c)$$

The electronic Hamiltonian H_e consists of a molecular resonance $|a\rangle$ with energy ε_a , the continuum states of the metal

nanoparticles $|k\rangle$ with energies ε_k , and the tunneling coupling v_{ak} between them. The molecular vibration H_v is approximated by a harmonic oscillator with vibrational frequency Ω .

In the resonance electron-vibration coupling, vibrational excitation is induced by the temporary occupation of the resonance state ($n_a = c_a^\dagger c_a$), resulting in vibrational motion on an excited state, which is described by a shifted harmonic oscillator with reaction coordinate q . The coupling constant λ for the linear electron-vibration interaction is determined by

$$\lambda = \sqrt{\frac{\hbar}{2\mu\Omega}} \frac{d}{dq} \varepsilon_a(q) \Big|_{q=q_0} \quad (3)$$

where μ is the reduced mass for the oscillator, and q_0 corresponds to the equilibrium position of the ground state. This term is mode-dependent, which may lead to mode-specific vibrational excitations in adsorbed molecules, as demonstrated in early calculations⁹¹ and recent experiments.^{18,71–75} Such a model Hamiltonian has been generally used to describe various dynamical processes in surface sciences, including vibrational damping,⁸⁵ electron energy loss spectroscopy,⁸⁶ dissociation induced by tunneling electrons,^{90,92} and femtosecond laser-induced desorption and dissociation.^{84,87–89}

Vibrational Transition Rates Induced by Plasmonic Hot Carriers. To describe plasmon-induced photocatalysis under CW laser irradiation, it is essential to consider the nonthermal hot carriers that are constantly generated during plasmonic damping. These hot carriers can couple to the molecule on a time scale given by the tunneling lifetime of the resonance state, which is typically a few femtoseconds.^{32–37} This is much shorter than the thermalization time on the picoseconds for hot carriers in metals and within the nanoparticles.^{60,93–96} The persistent generation of hot carriers by CW lasers makes it possible to maintain a nonthermal distribution on top of the thermal distribution governed by the Fermi–Dirac distribution $f_0(\varepsilon, T)$ with an electron temperature. The nonthermal distribution function under CW illumination is defined as²³

$$f_{\text{nth}}(\varepsilon) = \frac{\delta\rho(\varepsilon)}{\rho_{\text{DOS}}(\varepsilon)} \quad (4)$$

Here, $\rho_{\text{DOS}}(\varepsilon)$ is the electronic density of states of the nanoparticle, and $\delta\rho(\varepsilon)$ is the density response of hot carriers generated by Landau damping of plasmons, following Govorov^{50,55} as

$$\begin{aligned} \delta\rho(\varepsilon) = & 4e^2 \sum_{kk'} \frac{f_0(\varepsilon_{k'}) - f_0(\varepsilon_k)}{\Gamma_{kk}} \left| V_{kk'} \right|^2 \\ & \times \left[\frac{\Gamma_{kk'}}{(\hbar\omega - \varepsilon_k + \varepsilon_{k'})^2 + \Gamma_{kk'}^2} \right. \\ & \left. + \frac{\Gamma_{kk'}}{(\hbar\omega + \varepsilon_k - \varepsilon_{k'})^2 + \Gamma_{kk'}^2} \right] \delta(\varepsilon - \varepsilon_k) \end{aligned} \quad (5)$$

with $V_{kk'}$ as the optical transition matrix element, $\hbar\omega$ as the energy of incident photon, and $\Gamma_{kk'} = \Gamma_{kk} = \hbar/\tau$ as the relaxation matrix element in the relaxation time approximation. This f_{nth} can be treated on an equal footing with the equilibrium counterpart f_0 .

For an electron bath with a general distribution function $f(\varepsilon)$, the inelastic transition rate from vibrational state $|n\rangle$ to state $|n'\rangle$ of the ad molecule can be evaluated as^{86,87,90}

$$\begin{aligned}
 W_{n \rightarrow n'} &= \frac{4\Delta_a^2}{\pi\hbar} \int d\epsilon f(\epsilon) [1 - f(\epsilon + \delta\epsilon)] |T_{nm'}(\epsilon)|^2 \\
 &= \frac{4\Delta_a^2}{\pi\hbar} \int d\epsilon f(\epsilon) [1 - f(\epsilon + \delta\epsilon)] \\
 &\quad \times \left| \sum_m \frac{\langle n' | m \rangle \langle m | n \rangle}{\epsilon + \epsilon_n - \tilde{\epsilon}_a - \epsilon_m + i\Delta_a} \right|^2
 \end{aligned} \quad (6)$$

where $T_{nm'}$ is the transition amplitude between two bound levels $|n\rangle$ and $|n'\rangle$ via intermediate states $|m\rangle$, $\epsilon_n = n\hbar\Omega$ is the vibrational energy of state n , and $\delta\epsilon = \epsilon_n - \epsilon_{n'}$ is the energy transfer between electrons and the molecule. $\Delta_a = \sum_k \pi v_{ak}^2 \delta(\epsilon - \epsilon_k)$ is the broadening of molecular resonance, which effectively accounts for tunneling coupling with the electron bath. Its Hilbert transform $\Lambda_a = \sum_k \int d\epsilon' \frac{v_{ak}^2}{\epsilon - \epsilon'_k}$ yields the energy shift of the resonance state $\tilde{\epsilon}_a = \epsilon_a + \Lambda_a$.

$$F(m, n, n'; \beta) = \frac{\sqrt{n!n'!}}{m!} e^{-\beta^2} \beta^{n+n'+2m} \times \sum_{k_1=0}^{\min[n', m]} \sum_{k_2=0}^{\min[n, m]} \frac{\binom{m}{k_1} \binom{m}{k_2}}{(-\beta^2)^{k_1+k_2} (n' - k_1)! (n - k_2)!} \quad (8)$$

Eq 7 guarantees detailed balance between vibrational transitions, $W_{n \rightarrow n'}^{\text{th}}/W_{n' \rightarrow n}^{\text{th}} = \exp[(\epsilon_n - \epsilon_{n'})/k_B T_e]$. When the lattice and the electron bath are in equilibrium at the same temperature, eq 7 represents the vibrational transition rate without laser irradiation, namely, under dark condition.

To incorporate the nonthermal hot carriers generated by plasmon damping, the electron distribution function can be generalized to include the nonthermal term as²³

$$f(\epsilon, T) = f_0(\epsilon, T) + f_{\text{nth}}(\epsilon) \quad (9)$$

since these nonthermal hot carriers also participate in molecular scattering and vibrational excitation. In order to separate the thermal and nonthermal contributions, the product between distribution functions in eq 6 is partitioned into four parts,

$$\begin{aligned}
 &f(\epsilon)(1 - f(\epsilon + \delta\epsilon)) \\
 &= f_0(\epsilon)(1 - f_0(\epsilon + \delta\epsilon)) + f_{\text{nth}}(\epsilon)(1 - f_0(\epsilon + \delta\epsilon)) \\
 &\quad - f_0(\epsilon)f_{\text{nth}}(\epsilon + \delta\epsilon) - f_{\text{nth}}(\epsilon)f_{\text{nth}}(\epsilon + \delta\epsilon)
 \end{aligned} \quad (10)$$

Here, the first term corresponds to the contribution from the thermal distributions. Under normal laser intensity, f_{nth} should be much smaller compared to f_0 . Therefore, the last term can be neglected. The second and third terms correspond to the contributions from nonthermal hot electrons and hot holes, respectively. The non thermal vibrational transition rates can be reorganized as

$$\begin{aligned}
 W_{n \rightarrow n'}^{\text{nth}} &= W_{n \rightarrow n'}^{\text{HE}} + W_{n \rightarrow n'}^{\text{HH}} \\
 W_{n \rightarrow n'}^{\text{HE}} &= \frac{4\Delta_a^2}{\pi\hbar} \int d\epsilon f_{\text{nth}}(\epsilon) (1 - f_0(\epsilon + \delta\epsilon)) |T_{nm'}(\epsilon)|^2 \\
 W_{n \rightarrow n'}^{\text{HH}} &= -\frac{4\Delta_a^2}{\pi\hbar} \int d\epsilon f_0(\epsilon) f_{\text{nth}}(\epsilon + \delta\epsilon) |T_{nm'}(\epsilon)|^2
 \end{aligned}$$

Eq 11 can be numerically evaluated. This provides an unambiguous and concise way to calculate the nonthermal transition rates from hot electrons and holes, which was done by qualitatively dividing the distributions into three energy regimes.²³

For an electron bath with a thermal Fermi–Dirac distribution at an electron temperature T_e , it is not necessarily in equilibrium with the lattice or the environment in a dynamical process. The integration over the energy distribution can be evaluated in the wide-band approximation,^{86,87,90} using the analytic expression of the Franck–Condon factors between two displaced harmonic oscillators.⁹⁷ The result reads

$$\begin{aligned}
 W_{n \rightarrow n'}^{\text{th}} &= \frac{4\Delta_a^2 (n' - n) \Omega}{\pi} n_B(T_e, (n' - n)\hbar\Omega) \times \\
 &\quad \left| \sum_m \frac{F(m, n, n'; \beta)}{\epsilon_F + (n' + n - 2m)\hbar\Omega/2 - \tilde{\epsilon}_a + i\Delta_a} \right|^2
 \end{aligned} \quad (7)$$

where $n_B(T_e, \epsilon) = [\exp(\epsilon/k_B T_e) - 1]^{-1}$ is the Bose–Einstein distribution at T_e , $\beta = \lambda/(\hbar\Omega)$, and

Reaction Rates in DIET and DIMET Regimes. In the truncated harmonic oscillator approximation, molecular dissociation occurs when the vibrational energy surpasses the dissociation barrier. By considering the vibrational transitions from all bound states up to the dissociation level, n_d , the dissociation rate under laser excitation is given by

$$R_{\text{dis}} = \sum_{n=0}^{n_d-1} p_n(T) W_{n \rightarrow n_d} \quad (12)$$

where $p_n(T)$ is the thermal population of vibrational state n at temperature T . For reactions induced by single electronic transitions (DIET regime), their vibrational populations follow exactly the Bose–Einstein statistics at the electronic temperature T_e , which is assumed to be in thermal equilibrium with the environment.

The rate of dissociation in the DIET mechanism only accounts for a single inelastic scattering from the bound state. It does not include possible modifications of vibrational populations by multiple scatterings of nonthermal carriers in the DIMET regime. Experimentally, vibrational heating could occur under high laser irradiations⁹⁸ or in plasmonic gaps with strong local field enhancement.^{2,3,9–11} This can be described efficiently by introducing a modified vibrational temperature T_v , which in principle should be determined by solving the Pauli master equation.^{87,90}

A simple and approximate way to determine the vibrational temperature in the DIMET regime can be obtained by extracting the temperature from the vibrational transitions between the ground state $n = 0$ and the $n = 1$ excited state, i.e. $W_{0 \rightarrow 1}^{\text{tot}} = \Gamma_{\uparrow}^{\text{tot}}$ and $W_{1 \rightarrow 0}^{\text{tot}} = \Gamma_{\downarrow}^{\text{tot}}$, as

$$T_v = \frac{\hbar\Omega}{k_B \ln\left(\frac{\Gamma_{\downarrow}^{\text{tot}}}{\Gamma_{\uparrow}^{\text{tot}}}\right)} = \frac{\hbar\Omega}{k_B \ln\left(\frac{\Gamma_{\downarrow}^{\text{th}} + \Gamma_{\downarrow}^{\text{nth}}}{\Gamma_{\uparrow}^{\text{th}} + \Gamma_{\uparrow}^{\text{nth}}}\right)} \quad (13)$$

With the vibrational temperature, the dissociation rate within the DIMET mechanism can now be evaluated using the modified vibrational populations $p_n(T_v)$. We will later discuss the effect of the DIMET mechanism and make comparison

with the DIET mechanism,²³ as well as compare with other theoretical descriptions available in the literatures.^{2,84}

RESULTS AND DISCUSSIONS

Here, we apply the above model to study the vibrational excitation and dissociation of O₂ on AgNP, which has been intensively investigated experimentally.^{1,2} Upon adsorption, the O–O bond lies parallel to the surface,^{99–101} suggesting no direct coupling between the molecular dipole and the local field. Hence, direct photolysis by the electric field can be ruled out. To describe the electronic structures of AgNP, we adopt a jellium sphere model^{50–52} for the ground state spectrum of spherical nanoparticles with a diameter up to $D = 25$ nm and the Wigner–Seitz radius $r_s/r_B = 3.02$, where r_B is the Bohr radius. In the low-coverage limit, the effect of molecular adsorption on the plasmon properties, the so-called chemical interface damping,^{35,102–105} is minor and has been neglected. The adsorbate-specific parameters are extracted from first-principles calculations of O₂ chemisorbed on Ag(100),² with $\Delta_a = 0.6$ eV, $\varepsilon_a = 2.4$ eV corresponding to the $2\pi^*$ resonance of the O₂ on the Ag(100) surface formed by hot electron transfer, and $\hbar\Omega = 0.10$ eV being the vibrational energy of the adsorbed O–O stretch mode.

Hot Carrier Distribution. As the first step, the nonthermal distribution defined in eq 4 is evaluated as a function of wavelength and laser intensity. Figure 1a shows the energy and

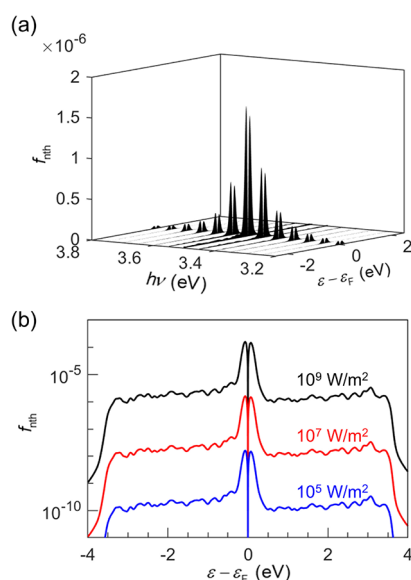


Figure 1. (a) Wavelength and (b) light intensity dependence of the nonthermal energy distributions of plasmonic hot carriers. A significant resonance enhancement appears at $h\nu = 3.5$ eV, corresponding to the plasmon resonance of a silver sphere with a diameter $D = 25$ nm. Based on the linear response framework, the hot carrier generation depends linearly on light intensity. The calculations are taken at $T = 300$ K, and $\tau = 100$ fs.

wavelength dependence of the nonthermal distribution function. When illuminated by light with a given energy $h\nu$, the hot carriers generated are essentially distributed within the energy range $(\varepsilon_F, \varepsilon_F + h\nu)$ for electrons and $(\varepsilon_F - h\nu, \varepsilon_F)$ for holes, respectively. Both distributions of electrons and holes are plotted by the absolute magnitude. For a given particle size D and carrier lifetime τ , the nonthermal carriers are distributed predominantly near the Fermi level due to the available

thermal electron–hole pairs near the Fermi surface. The hot carriers are therefore affected by the populations of thermal electron–hole pairs during Landau damping. Apart from this thermal character, there are purely nonthermal distributions at energies far from the Fermi level. Increasing the carrier lifetime or reducing the nanoparticle size favors hot carrier generation and thus enhances the nonthermal distributions.⁵¹ In the dependence of photon energy, a clear resonance enhancement can be observed at $h\nu \sim 3.5$ eV, which coincides with the calculated plasmon resonance $\hbar\omega_p$ of the AgNP at the given diameter.¹⁰⁶ This resonance effect confirms that plasmon excitation is dominant in hot carrier generation.

Figure 1b shows the hot carrier distributions as a function of the light intensity. These distributions have the same energy profiles. The magnitude of the distributions depends linearly on the light intensity I_0 , as expected from linear response theory.⁴⁰ Under near-resonant excitation, the local field experienced by the conduction electrons is dominated by the plasmonic field, whose intensity scales linearly with that of the incident light.^{50–52}

Figure 2a shows, in more detail, the total hot carrier distribution function at $T = 300$ K including both the thermal

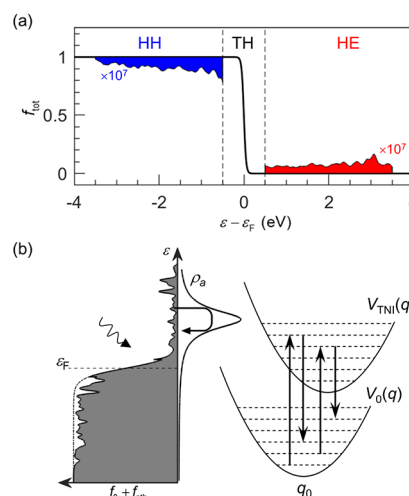


Figure 2. (a) Total electronic energy distribution at $T = 300$ K and $I_0 = 10^7$ W/m². Carriers are segmented into three regions. The TH region around the Fermi level contains mostly the thermal carriers, while the HH and HE regions consist of hot holes and hot electrons, respectively. The nonthermal characters are colored for clarification. (b) Schematic of a unified treatment of thermal and nonthermal hot carrier distributions in the vibrational heating mechanism.

and the nonthermal distributions. The overall distribution is dominated by the thermal distribution, as expected. Nonthermal distributions are substantially smaller in magnitude for low-energy electrons and holes near the Fermi level. However, away from the Fermi level, the thermal distributions decay exponentially, while the nonthermal distributions do not. This implies that the high-energy distributions should always be dominated by the nonthermal electron–hole pairs. To help understand the different contributions from the thermal and nonthermal carriers, we could qualitatively divide the total distribution function into three regions. The thermal (TH) region near the Fermi level contains both thermal and nonthermal components but is overwhelmingly dominated by the thermal carriers. The hot hole (HH) and hot electron (HE) regions predominantly consist of hot holes and hot

electrons, respectively. The insets are close ups of distributions in the HH and HE regions.

Rates of Vibrational Transitions. To explore how the nonthermal hot carriers affect the vibrational excitation of the molecules adsorbed on the nanoparticle surface, whose general picture involving tunneling coupling is schematically shown in Figure 2b, we plot in Figure 3a the rate of vibrational excitation

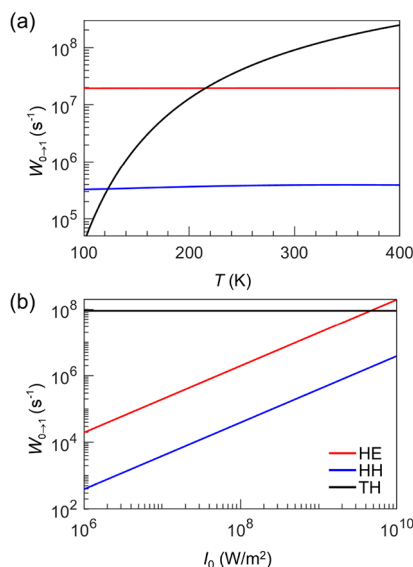


Figure 3. (a) Temperature and (b) light intensity dependence of the vibrational excitation rate $W_{0 \rightarrow 1}$ with contributions from hot electrons (red lines), hot holes (blue lines), and thermal carriers (black lines). The nonthermal carriers are efficient in promoting the activation of molecular vibrations in the low-temperature and/or high-light-intensity regime.

$W_{0 \rightarrow 1}$ as a function of temperature, with separate contributions from hot electrons (red line), hot holes (blue line), and thermal carriers (black line). The thermal contribution increases with temperature, while those of hot electrons and hot holes are temperature-independent due to their non-thermal characters. Excitation by nonthermal hot carriers dominates at low temperatures and is outweighed by the thermal contribution at temperatures above 220 K. Moreover, the unoccupied O₂ 2 π^* resonance obviously favors vibrational coupling with hot electrons rather than hot holes, leading to larger vibrational excitation rates for the hot electrons.

Figure 3b shows the light intensity dependence of $W_{0 \rightarrow 1}$ at a fixed temperature of 300 K. Contributions from different carriers are presented in the same way as shown in Figure 3a. Here, the nonthermal contributions increase linearly with the light intensity, as expected from linear response theory. It is clear that thermal excitation dominates $W_{0 \rightarrow 1}$ under weak illumination and is overtaken by hot electrons for light intensities higher than $\sim 4 \times 10^9$ W/m². For vibrational transitions involving larger energy transfers, nonthermal hot carriers can dominate vibrational excitations at much lower light intensities.

Dissociation Rate and Vibrational Heating. We next analyze the dissociation rate of O₂ on AgNP. A laser with $h\nu = 3.5$ eV is used for resonance plasmon excitation, and the dissociation level is taken as $n_d = 6$. In our previous work,²³ only the DIET regime with a fixed light intensity has been considered. However, vibrational heating has been reported at

high light intensities in the same system.² To account for the modified vibrational distribution induced by multiple electronic scatterings, a vibrational temperature approximation^{87,88} can be introduced. In Figure 4a, the vibrational temperatures

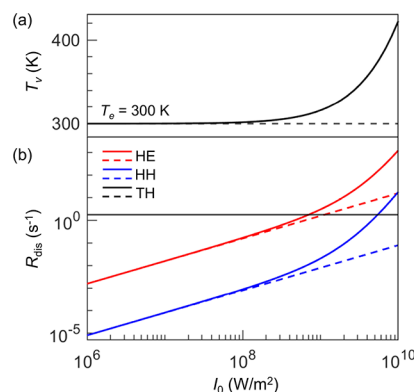


Figure 4. (a) Light intensity dependence of the vibrational temperature (solid lines) under resonant illumination. As compared to the electronic temperature (dashed lines), dramatic vibrational heating of adsorbate can be observed, especially at high values of light intensity. (b) Dissociation rates as a function of light intensity in the DIMET regime (solid lines) and are compared to the corresponding DIET curves (dashed lines). The transition from a linear to a superlinear dependence can be observed, indicating the onset of vibrational heating.

T_v given by eq 13 are displayed as a function of light intensity at a fixed environmental temperature $T_{env} = T_e = 300$ K. As shown in Figure 3b, the vibrational excitations are still dominated by thermal activation at low light intensities. The vibrational temperatures are thus in equilibrium with the electronic temperature. However, as the light intensity increases, the populations on higher vibrational states are increased consequently, which result in elevated vibrational temperatures. Indeed, mode-specific vibrational temperatures in adsorbed molecules have been reported using Raman thermometry^{18,71–75} and have been suggested as a signature of the hot carrier mechanism in plasmonic photocatalysis.

The modified vibrational temperature leads to enhanced rates of dissociation, especially in the DIMET regime. Figure 4b shows the light intensity dependence of the dissociation rates with separate contributions from thermal and nonthermal hot carriers. Both the DIET (dashed lines) and DIMET (solid lines) mechanisms are shown. For the thermal channel (TH), the vibrational temperature remains unperturbed ($T_v = T_e$), resulting in identical rates in both mechanisms. The thermal electronic distribution is independent of light intensity, leading to a constant dissociation rate. In contrast, nonthermal hot carriers lead to distinct intensity dependence of the dissociation rates. At low intensities, dissociation is governed by the DIET mechanism with a linear intensity dependence. As the light intensity increases, a transition from the linear to superlinear dependence occurs due to the onset of vibrational heating. The superlinearity results from the additional vibrational transitions from higher vibrational states and elevated vibrational populations.^{84,86–90} This effect can be rationalized as a reduced dissociation barrier^{1–3,10–12} without considering the modified vibrational temperatures. However, the microscopic description of vibrational temperature presented here is more physical and aligns with experimental

observations of elevated and mode-dependent vibrational temperatures.^{18,71–75}

The light intensity dependence of the dissociation rate suggests that the thermal contribution dominates only under low light irradiation and is gradually prevailed by the nonthermal contribution at increasing light intensities. Such an unambiguous distinction between the thermal and non-thermal effects is crucial in understanding the mechanism involved, which has not been achieved in previous models.^{2,84} This benefits from a unified treatment of the thermal and nonthermal hot carrier distributions. Moreover, the non-thermal hot electrons are found to be more favorable to trigger molecular dissociation, with the corresponding rate being several orders of magnitude higher than the hot holes. This is consistent with the vibrational transition rates shown in Figure 3, which originates from the better energy alignment between hot electrons and molecular resonance. We note that recent experiments proposed an alternative hot hole mechanism for single O₂ dissociation in a tunneling configuration,^{107,108} which is interesting and deserves future investigation. Therefore, Figure 4b suggests that at relatively high light intensities, nonthermal hot carriers can greatly promote and even dominate plasmonic photocatalysis, and the reaction mechanism evolves from single to multiple electronic transitions at the onset of significant vibrational heating.

Figure 5 shows the dissociation rate as a function of temperature in the vibrational heating mechanism. The

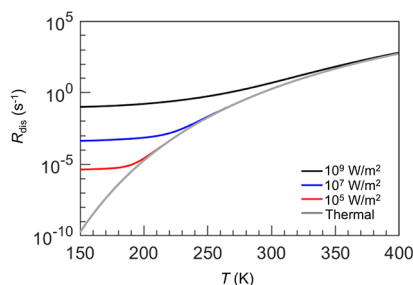


Figure 5. Temperature dependence of the total dissociation rate at different light intensities under resonant excitation. The nonthermal contributions are dominant in the low-temperature regime as compared to the thermal reaction limit (gray solid line). All calculations are taken at $n_d = 6$, and $\tau = 100$ fs.

thermal rate (Thermal) corresponds to a background dissociation rate under dark condition. It essentially follows the Arrhenius law. Plasmonic hot carriers under light irradiation open a nonthermal channel of dissociation that increases with light intensity. Such a nonthermal enhancement is more dramatic in the low-temperature regime, where thermal carrier excitation is suppressed and the dynamic activation to the dissociation level is thus only accessible through nonthermal hot carriers. As the temperature increases, the thermal excitation of higher vibrational states becomes more efficient. It effectively diminishes its nonthermal counterpart. The results here are in line with earlier data in the DIET mechanism²³ and expose additional light intensity dependence in the vibrational heating mechanism. Figure 5 indicates that plasmonic hot carriers can promote photodissociation mostly in the low-temperature and high-light-intensity regimes, where vibrational heating induced by nonthermal hot carriers becomes efficient and dominant.

While the model captures the essential features of non-thermal hot carriers in the rate of plasmonic photodissociation and its transition from linear to superlinear light intensity dependence, the calculated threshold ($\sim 10^8$ W/m²) of the transition is considerably higher than the light intensity measured in the experiment ($\sim 10^3$ W/m²).² This difference between theory and experiment could be attributed to the extra local field enhancement present at the plasmonic gaps in the experiment. Typically, the experiment was performed on an ensemble of nanocubes, where the photodissociation mostly took place at hot spots in narrow plasmonic gaps.² The local field therein is substantially higher than the surface field on a single spherical nanoparticle treated in our calculations.¹⁰⁹ For instance, the field enhancement at the hot spot of the nanoparticle dimer can be more than 3 orders of magnitude higher than that near an individual nanoparticle.² This local field argument is also consistent with the experimental observation that a single nanoparticle did not yield photodissociation at the same experimental conditions.² In addition, dynamics beyond the one-dimensional harmonic oscillator, and a possible inhomogeneous density distribution of hot carriers,⁶⁴ which are neglected in our model but may be present in the larger nanoparticles used in the experiment,^{7,14,17} may be additional factors contributing to the discrepancy.

Which Hot Carriers Are Operative? The answer to this question is relevant to the mechanism of plasmonic photochemistry. Although the photodissociation of O₂ has been analyzed in a similar model,^{2,84} it did not explicitly account for the hot carrier distributions and their energy-dependent activation to a molecular resonance. Instead, it was assumed that a single hot carrier at the plasmon resonance energy is exclusively involved in the scattering event. To gain insight into which carriers are important for photocatalysis, we have segmented the dissociation rates in the hot carrier spectrum with an energy step of 0.2 eV. As shown in the upper panel of Figure 6, in the thermal regime, only the carriers near the Fermi level provide the dominant contributions to molecular dissociation. This results from the electron–hole pair distribution factor, $f(\epsilon)[1 - f(\epsilon + \delta\epsilon)]$ in eq 6, which is peaked at the Fermi energy of the thermal electronic bath.

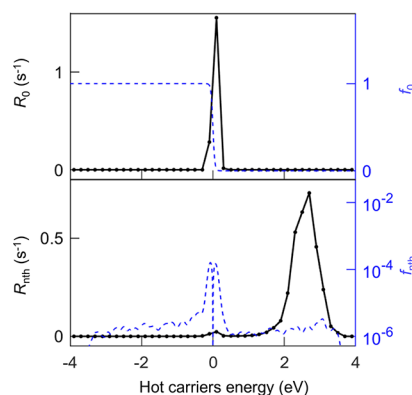


Figure 6. Thermal and nonthermal contributions to reaction rates obtained in different energy regions of the hot carriers spectrum. While the thermal contributions are dominated by hot carriers close to the Fermi level, nonthermal hot carriers with a broad energy range from near the molecular resonance to the plasmon resonance provide comparable contributions. Parameters used in the calculations are $h\nu = 3.5$ eV, $T = 300$ K, $I_0 = 10^9$ W/m², and $\tau = 100$ fs.

Therefore, the low-energy electron–hole pairs near the Fermi level are the most active carriers in activating the molecules through an off-resonance excitation mechanism. In contrast, the nonthermal distribution f_{nth} has appreciable populations in the high-energy regime. These energetic carriers better align with the $2\pi^*$ resonance of the O_2 molecules, dominating the contributions to molecular dissociation through a resonance electron-molecule excitation.

A detailed look at the resonance dissociation peak in the lower panel of Figure 6 suggests that the hot carriers involved cannot be attributed to a single electron excitation with energy equals to neither the plasmon energy (3.5 eV^{106}) nor the molecular resonance (2.4 eV^2). Instead, it shows a broad energy distribution from 1.8 to 3.6 eV, demonstrating the combined effects of the molecular resonance and the nonthermal hot carrier distributions. This suggests that a proper treatment of the energy-dependent coupling with the hot electron bath is important to understand the mechanism and is an essential step beyond a single-electron scattering picture.^{2,84} The unified description of the thermal and nonthermal hot carriers in our model provides a concise theoretical framework and quantitative assessment of their relative contributions in the coupling with molecular resonance. It offers deeper insight into the mechanism of plasmonic photocatalysis within a well-defined model.

CONCLUSIONS

Based on the Anderson–Newns model of resonance electron–vibration coupling and an explicit derivation of the nonthermal hot carrier distribution, we have presented a unified description of vibrational heating and dissociation induced by plasmonic hot carriers, with the focus on the mechanism of plasmon-induced photocatalysis. As an application of the model, we have revisited the photodissociation of O_2 adsorbed on AgNP and systematically examined the dissociation rate as functions of temperature and light intensity. Treating the nonthermal and thermal distributions on equal footing has allowed us to gain a quantitative assessment of the contributions from nonthermal carriers in comparison with that from thermal carriers. The results demonstrate that a small fraction of population by energetic nonthermal carriers is sufficient to greatly enhance the vibrational excitation, thus promoting catalytic dissociation, especially in the low-temperature or high-light-intensity regime. Furthermore, single electronic scattering dominates the dissociation under weak excitation; vibrational heating induced by multiple electronic scatterings outweighs as the light intensity increases, giving a linear-to-superlinear dependence of the dissociation rate. Our model captures the essential physics underlying the mechanism of plasmonic catalysis and provides a unified theoretical framework to describe hot carrier photochemistry in both the thermal and nonthermal regimes.

AUTHOR INFORMATION

Corresponding Author

Shiwu Gao – Beijing Computational Science Research Center, Beijing 100193, China; orcid.org/0000-0002-4530-5022; Email: swgao@csrcc.ac.cn

Authors

Yu Chen – Beijing Computational Science Research Center, Beijing 100193, China

Shengxiang Wu – Beijing Computational Science Research Center, Beijing 100193, China

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.jpcc.4c08348>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (11934003, 12393831, and U2230402).

REFERENCES

- (1) Christopher, P.; Xin, H.; Linic, S. Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures. *Nat. Chem.* **2011**, *3*, 467–472.
- (2) Christopher, P.; Xin, H.; Marimuthu, A.; Linic, S. Singular characteristics and unique chemical bond activation mechanisms of photocatalytic reactions on plasmonic nanostructures. *Nat. Mater.* **2012**, *11*, 1044–1050.
- (3) Mukherjee, S.; Libisch, F.; Large, N.; Neumann, O.; Brown, L. V.; Cheng, J.; Lassiter, J. B.; Carter, E. A.; Nordlander, P.; Halas, N. J. Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of on Au. *Nano Lett.* **2013**, *13*, 240–247.
- (4) Mukherjee, S.; Zhou, L.; Goodman, A. M.; Large, N.; Ayala-Orozco, C.; Zhang, Y.; Nordlander, P.; Halas, N. J. Hot-Electron-Induced Dissociation of on Gold Nanoparticles Supported on Si. *J. Am. Chem. Soc.* **2014**, *136*, 64–67.
- (5) Mubeen, S.; Lee, J.; Singh, N.; Krämer, S.; Stucky, G. D.; Moskovits, M. An autonomous photosynthetic device in which all charge carriers derive from surface plasmons. *Nat. Nanotechnol.* **2013**, *8*, 247–251.
- (6) Aslam, U.; Chavez, S.; Linic, S. Controlling energy flow in multimetallic nanostructures for plasmonic catalysis. *Nat. Nanotechnol.* **2017**, *12*, 1000–1005.
- (7) Cortés, E.; Xie, W.; Cambiasso, J.; Jermyn, A. S.; Sundaraman, R.; Narang, P.; Schlücker, S.; Maier, S. A. Plasmonic hot electron transport drives nano-localized chemistry. *Nat. Commun.* **2017**, *8*, 14880.
- (8) Hu, C.; Chen, X.; Jin, J.; Han, Y.; Chen, S.; Ju, H.; Cai, J.; Qiu, Y.; Gao, C.; Wang, C.; et al. Surface Plasmon Enabling Nitrogen Fixation in Pure Water through a Dissociative Mechanism under Mild Conditions. *J. Am. Chem. Soc.* **2019**, *141*, 7807–7814.
- (9) Swearer, D. F.; Zhao, H.; Zhou, L.; Zhang, C.; Robotjazi, H.; Martinez, J. M.; Krauter, C. M.; Yazdi, S.; McClain, M. J.; Ringe, E.; et al. Heterometallic antenna-reactor complexes for photocatalysis. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 8916.
- (10) Swearer, D. F.; Robotjazi, H.; Martinez, J. M. P.; Zhang, M.; Zhou, L.; Carter, E. A.; Nordlander, P.; Halas, N. J. Plasmonic Photocatalysis of Nitrous Oxide into and Using Aluminum-Iridium Antenna-Reactor Nanoparticles. *ACS Nano* **2019**, *13*, 8076–8086.
- (11) Robotjazi, H.; Bao, J. L.; Zhang, M.; Zhou, L.; Christopher, P.; Carter, E. A.; Nordlander, P.; Halas, N. J. Plasmon-driven carbon–fluorine (C(s)–F) bond activation with mechanistic insights into hot-carrier-mediated pathways. *Nat. Catal.* **2020**, *3*, 564–573.
- (12) Zhou, L.; Swearer, D. F.; Zhang, C.; Robotjazi, H.; Zhao, H.; Henderson, L.; Dong, L.; Christopher, P.; Carter, E. A.; Nordlander, P.; et al. Quantifying hot carrier and thermal contributions in plasmonic photocatalysis. *Science* **2018**, *362*, 69.
- (13) Stefancu, A.; Gargiulo, J.; Laifersky, G.; Auguier, B.; Chiş, V.; Le Ru, E. C.; Liu, M.; Leopold, N.; Cortés, E. Interface-Dependent Selectivity in Plasmon-Driven Chemical Reactions. *ACS Nano* **2023**, *17*, 3119–3127.
- (14) Ezendam, S.; Gargiulo, J.; Sousa-Castillo, A.; Lee, J. B.; Nam, Y. S.; Maier, S. A.; Cortés, E. Spatial Distributions of Single-Molecule Reactivity in Plasmonic Catalysis. *ACS Nano* **2024**, *18*, 451–460.

- (15) Kim, Y.; Smith, J. G.; Jain, P. K. Harvesting multiple electron-hole pairs generated through plasmonic excitation of Au nanoparticles. *Nat. Chem.* **2018**, *10*, 763–769.
- (16) Zhou, L.; Martinez, J. M. P.; Finzel, J.; Zhang, C.; Swearer, D. F.; Tian, S.; Robatjazi, H.; Lou, M.; Dong, L.; Henderson, L.; et al. Light-driven methane dry reforming with single atomic site antenna-reactor plasmonic photocatalysts. *Nat. Energy* **2020**, *5*, 61–70.
- (17) Kang, Y.; Joao, S. M.; Lin, R.; Liu, K.; Zhu, L.; Fu, J.; Cheong, W. M.; Lee, S.; Frank, K.; Nickel, B.; et al. Effect of crystal facets in plasmonic catalysis. *Nat. Commun.* **2024**, *15*, 3923.
- (18) Boerigter, C.; Campana, R.; Morabito, M.; Linic, S. Evidence and implications of direct charge excitation as the dominant mechanism in plasmon-mediated photocatalysis. *Nat. Commun.* **2016**, *7*, 10545.
- (19) Kazuma, E.; Jung, J.; Ueba, H.; Trenary, M.; Kim, Y. Real-space and real-time observation of a plasmon-induced chemical reaction of a single molecule. *Science* **2018**, *360*, 521.
- (20) Seemala, B.; Therrien, A. J.; Lou, M.; Li, K.; Finzel, J. P.; Qi, J.; Nordlander, P.; Christopher, P. Plasmon-Mediated Catalytic Dissociation on Ag Nanostructures: Hot Electrons or Near Fields? *ACS Energy Lett.* **2019**, *4*, 1803–1809.
- (21) Dubi, Y.; Un, I. W.; Sivan, Y. Thermal effects - an alternative mechanism for plasmon-assisted photocatalysis. *Chem. Sci.* **2020**, *11*, 5017.
- (22) Un, I. W.; Dubi, Y.; Sivan, Y. Photothermal nonlinearity in plasmon-assisted photocatalysis. *Nanoscale* **2022**, *14*, S022.
- (23) Wu, S.; Chen, Y.; Gao, S. Plasmonic Photocatalysis with Nonthermalized Hot Carriers. *Phys. Rev. Lett.* **2022**, *129*, No. 086801. Due to a flaw in the numerical implementation, the laser intensity used here was underestimated by 3 orders of magnitude.
- (24) Yan, L.; Wang, F.; Meng, S. Quantum Mode Selectivity of Plasmon-Induced Water Splitting on Gold Nanoparticles. *ACS Nano* **2016**, *10*, 5452–5458.
- (25) Zhang, Y.; Yan, L.; Guan, M.; Chen, D.; Xu, Z.; Guo, H.; Hu, S.; Zhang, S.; Liu, X.; Guo, Z.; et al. Indirect to Direct Charge Transfer Transition in Plasmon-Enabled C Photoreduction. *Adv. Sci.* **2022**, *9*, No. e2102978.
- (26) Zhang, Y.; Nelson, T.; Tretiak, S.; Guo, H.; Schatz, G. C. Plasmonic Hot-Carrier-Mediated Tunable Photochemical Reactions. *ACS Nano* **2018**, *12*, 8415–8422.
- (27) Wu, Q.; Zhou, L.; Schatz, G. C.; Zhang, Y.; Guo, H. Mechanistic Insights into Photocatalyzed Dissociation on Au Clusters. *J. Am. Chem. Soc.* **2020**, *142*, 13090–13101.
- (28) Aslam, U.; Rao, V. G.; Chavez, S.; Linic, S. Catalytic conversion of solar to chemical energy on plasmonic metal nanostructures. *Nat. Catal.* **2018**, *1*, 656–665.
- (29) Zhan, C.; Moskovits, M.; Tian, Z.-Q. Recent Progress and Prospects in Plasmon-Mediated Chemical Reaction. *Matter* **2020**, *3*, 42–56.
- (30) Furube, A.; Du, L.; Hara, K.; Katoh, R.; Tachiya, M. Ultrafast plasmon-induced electron transfer from gold nanodots into Ti nanoparticles. *J. Am. Chem. Soc.* **2007**, *129*, 14852–14853.
- (31) Wu, K.; Rodriguez-Cordoba, W. E.; Yang, Y.; Lian, T. Plasmon-induced hot electron transfer from the Au tip to CdS rod in CdS-Au nanoheterostructures. *Nano Lett.* **2013**, *13*, 5255–5263.
- (32) Wu, K.; Chen, J.; McBride, J. R.; Lian, T. Efficient hot-electron transfer by a plasmon-induced interfacial charge-transfer transition. *Science* **2015**, *349*, 632.
- (33) Tagliabue, G.; DuChene, J. S.; Abdellah, M.; Habib, A.; Gosztola, D. J.; Hattori, Y.; Cheng, W.-H.; Zheng, K.; Canton, S. E.; Sundararaman, R.; et al. Ultrafast hot-hole injection modifies hot-electron dynamics in Au/p-GaN heterostructures. *Nat. Mater.* **2020**, *19*, 1312–1318.
- (34) Zhang, Q.; Li, W.; Zhao, R.; Tang, P.; Zhao, J.; Wu, G.; Chen, X.; Hu, M.; Yuan, K.; Li, J.; et al. Real-time observation of two distinctive non-thermalized hot electron dynamics at MXene/molecule interfaces. *Nat. Commun.* **2024**, *15*, 4406.
- (35) Ostovar, B.; Lee, S. A.; Mehmood, A.; Farrell, K.; Searles, E. K.; Bourgeois, B.; Chiang, W. Y.; Misiura, A.; Gross, N.; Al-Zubeidi, A.; et al. The role of the plasmon in interfacial charge transfer. *Sci. Adv.* **2024**, *10*, No. eadp3353.
- (36) Ma, J.; Gao, S. Plasmon-Induced Electron–Hole Separation at the Ag/Ti(110) Interface. *ACS Nano* **2019**, *13*, 13658–13667.
- (37) Ma, J.; Zhang, X.; Gao, S. Tunable electron and hole injection channels at plasmonic Al–Ti interfaces. *Nanoscale* **2021**, *13*, 14073.
- (38) Kumar, P. V.; Rossi, T. P.; Kuisma, M.; Erhart, P.; Norris, D. J. Direct hot-carrier transfer in plasmonic catalysis. *Faraday Discuss.* **2019**, *214*, 189–197.
- (39) Kumar, P. V.; Rossi, T. P.; Marti-Dafcik, D.; Reichmuth, D.; Kuisma, M.; Erhart, P.; Puska, M. J.; Norris, D. J. Plasmon-Induced Direct Hot-Carrier Transfer at Metal–Acceptor Interfaces. *ACS Nano* **2019**, *13*, 3188–3195.
- (40) Dubi, Y.; Sivan, Y. “Hot” electrons in metallic nanostructures—non-thermal carriers or heating? *Light Sci. Appl.* **2019**, *8*, 89.
- (41) Baffou, G.; Bordacchini, I.; Baldi, A.; Quidant, R. Simple experimental procedures to distinguish photothermal from hot-carrier processes in plasmonics. *Light Sci. Appl.* **2020**, *9*, 108.
- (42) Govorov, A. O.; Zhang, W.; Skeini, T.; Richardson, H.; Lee, J.; Kotov, N. A. Gold nanoparticle ensembles as heaters and actuators: melting and collective plasmon resonances. *Nanoscale Res. Lett.* **2006**, *1*, 84–90.
- (43) Baffou, G.; Berto, P.; Bermúdez Ureña, E.; Quidant, R.; Monneret, S.; Polleux, J.; Rigneault, H. Photoinduced Heating of Nanoparticle Arrays. *ACS Nano* **2013**, *7*, 6478–6488.
- (44) Zhou, L.; Lou, M.; Bao, J. L.; Zhang, C.; Liu, J. G.; Martinez, J. M. P.; Tian, S.; Yuan, L.; Swearer, D. F.; Robatjazi, H.; et al. Hot carrier multiplication in plasmonic photocatalysis. *Proc. Natl. Acad. Sci. U. S. A.* **2021**, *118*, No. e2022109118.
- (45) Zhang, X.; Li, X.; Reish, M. E.; Zhang, D.; Su, N. Q.; Gutierrez, Y.; Moreno, F.; Yang, W.; Everitt, H. O.; Liu, J. Plasmon-Enhanced Catalysis: Distinguishing Thermal and Nonthermal Effects. *Nano Lett.* **2018**, *18*, 1714–1723.
- (46) Zhan, C.; Liu, B. W.; Huang, Y. F.; Hu, S.; Ren, B.; Moskovits, M.; Tian, Z. Q. Disentangling charge carrier from photothermal effects in plasmonic metal nanostructures. *Nat. Commun.* **2019**, *10*, 2671.
- (47) Zhan, C.; Wang, Q.-X.; Yi, J.; Chen, L.; Wu, D.-Y.; Wang, Y.; Xie, Z.-X.; Moskovits, M.; Tian, Z.-Q. Plasmonic nanoreactors regulating selective oxidation by energetic electrons and nanoconfined thermal fields. *Sci. Adv.* **2021**, *7*, No. eabf0962.
- (48) Kamarudheen, R.; Aalbers, G. J. W.; Hamans, R. F.; Kamp, L. P. J.; Baldi, A. Distinguishing Among All Possible Activation Mechanisms of a Plasmon-Driven Chemical Reaction. *ACS Energy Lett.* **2020**, *5*, 2605–2613.
- (49) Miyar, R.; Un, I. W.; Har Lavan, S.; Dubi, Y.; Baraban, J. H.; Sivan, Y.; Rosen, B. A. Disentangling Plasmonic Enhancement of Electronic and Thermal Effects in Catalysis Using In Operando X-ray Diffraction. *ACS Catal.* **2025**, *15*, 2359–2366.
- (50) Govorov, A. O.; Zhang, H.; Gun'ko, Y. K. Theory of Photoionization of Hot Plasmonic Carriers from Metal Nanostructures into Semiconductors and Surface Molecules. *J. Phys. Chem. C* **2013**, *117*, 16616–16631.
- (51) Manjavacas, A.; Liu, J. G.; Kulkarni, V.; Nordlander, P. Plasmon-Induced Hot Carriers in Metallic Nanoparticles. *ACS Nano* **2014**, *8*, 7630–7638.
- (52) Liu, J. G.; Zhang, H.; Link, S.; Nordlander, P. Relaxation of Plasmon-Induced Hot Carriers. *ACS Photonics* **2018**, *5*, 2584–2595.
- (53) Saavedra, J. R. M.; Asenjo-Garcia, A.; García de Abajo, F. J. Hot-Electron Dynamics and Thermalization in Small Metallic Nanoparticles. *ACS Photonics* **2016**, *3*, 1637–1646.
- (54) Besteiro, L. V.; Kong, X.-T.; Wang, Z.; Hartland, G.; Govorov, A. O. Understanding Hot-Electron Generation and Plasmon Relaxation in Metal Nanocrystals: Quantum and Classical Mechanisms. *ACS Photonics* **2017**, *4*, 2759–2781.
- (55) Govorov, A. O.; Zhang, H. Kinetic Density Functional Theory for Plasmonic Nanostructures: Breaking of the Plasmon Peak in the Quantum Regime and Generation of Hot Electrons. *J. Phys. Chem. C* **2015**, *119*, 6181–6194.

- (56) Santiago, E. Y.; Besteiro, L. V.; Kong, X.-T.; Correa-Duarte, M. A.; Wang, Z.; Govorov, A. O. Efficiency of Hot-Electron Generation in Plasmonic Nanocrystals with Complex Shapes: Surface-Induced Scattering, Hot Spots, and Interband Transitions. *ACS Photonics* **2020**, *7*, 2807–2824.
- (57) Bernardi, M.; Mustafa, J.; Neaton, J. B.; Louie, S. G. Theory and computation of hot carriers generated by surface plasmon polaritons in noble metals. *Nat. Commun.* **2015**, *6*, 7044.
- (58) Sundararaman, R.; Narang, P.; Jermyn, A. S.; Goddard, W. A., III; Atwater, H. A. Theoretical predictions for hot-carrier generation from surface plasmon decay. *Nat. Commun.* **2014**, *5*, 5788.
- (59) Brown, A. M.; Sundararaman, R.; Narang, P.; Goddard, W. A., III; Atwater, H. A. Nonradiative Plasmon Decay and Hot Carrier Dynamics: Effects of Phonons, Surfaces, and Geometry. *ACS Nano* **2016**, *10*, 957–966.
- (60) Brown, A. M.; Sundararaman, R.; Narang, P.; Schwartzberg, A. M.; Goddard, W. A.; Atwater, H. A. Experimental and *Ab Initio* Ultrafast Carrier Dynamics in Plasmonic Nanoparticles. *Phys. Rev. Lett.* **2017**, *118*, No. 087401.
- (61) Román Castellanos, L.; Hess, O.; Lischner, J. Single plasmon hot carrier generation in metallic nanoparticles. *Commun. Phys.* **2019**, *2*, 47.
- (62) Jin, H.; Kahk, J. M.; Papaconstantopoulos, D. A.; Ferreira, A.; Lischner, J. Plasmon-Induced Hot Carriers from Interband and Intraband Transitions in Large Noble Metal Nanoparticles. *PRX Energy* **2022**, *1*, No. 013006.
- (63) João, S. M.; Jin, H.; Lischner, J. C. Atomistic Theory of Hot-Carrier Relaxation in Large Plasmonic Nanoparticles. *J. Phys. Chem. C* **2023**, *127*, 23296–23302.
- (64) Rossi, T. P.; Erhart, P.; Kuisma, M. Hot-Carrier Generation in Plasmonic Nanoparticles: The Importance of Atomic Structure. *ACS Nano* **2020**, *14*, 9963–9971.
- (65) Fojt, J.; Rossi, T. P.; Kumar, P. V.; Erhart, P. Tailoring Hot-Carrier Distributions of Plasmonic Nanostructures through Surface Alloying. *ACS Nano* **2024**, *18*, 6398–6405.
- (66) Heilpern, T.; Manjare, M.; Govorov, A. O.; Wiederrecht, G. P.; Gray, S. K.; Harutyunyan, H. Determination of hot carrier energy distributions from inversion of ultrafast pump-probe reflectivity measurements. *Nat. Commun.* **2018**, *9*, 1853.
- (67) Cushing, S. K.; Chen, C.-J.; Dong, C. L.; Kong, X.-T.; Govorov, A. O.; Liu, R.-S.; Wu, N. Tunable Nonthermal Distribution of Hot Electrons in a Semiconductor Injected from a Plasmonic Gold Nanostructure. *ACS Nano* **2018**, *12*, 7117–7126.
- (68) Reddy, H.; Wang, K.; Kudyshev, Z.; Zhu, L.; Yan, S.; Vezzoli, A.; Higgins, S. J.; Gavini, V.; Boltasseva, A.; Reddy, P.; et al. Determining plasmonic hot-carrier energy distributions via single-molecule transport measurements. *Science* **2020**, *369*, 423.
- (69) Budai, J.; Papa, Z.; Petrik, P.; Dombi, P. Ultrasensitive probing of plasmonic hot electron occupancies. *Nat. Commun.* **2022**, *13*, 6695.
- (70) Lin, C.; Krecinic, F.; Yoshino, H.; Hammud, A.; Pan, A.; Wolf, M.; Müller, M.; Kumagai, T. Continuous-Wave Multiphoton-Induced Electron Transfer in Tunnel Junctions Driven by Intense Plasmonic Fields. *ACS Photonics* **2023**, *10*, 3637–3646.
- (71) Shin, H. H.; Jeong, J.; Nam, Y.; Lee, K. S.; Yeon, G. J.; Lee, H.; Lee, S. Y.; Park, S.; Park, H.; Lee, J. Y.; et al. Vibrationally Hot Reactants in a Plasmon-Assisted Chemical Reaction. *J. Am. Chem. Soc.* **2023**, *145*, 12264–12274.
- (72) Jeong, J.; Shin, H.-H.; Kim, Z. H. Unveiling the Mechanism of Plasmon Photocatalysis via Multiquantum Vibrational Excitation. *ACS Nano* **2024**, *18*, 25290–25301.
- (73) Boerigter, C.; Aslam, U.; Linic, S. Mechanism of Charge Transfer from Plasmonic Nanostructures to Chemically Attached Materials. *ACS Nano* **2016**, *10*, 6108–6115.
- (74) Keller, E. L.; Frontiera, R. R. Ultrafast Nanoscale Raman Thermometry Proves Heating Is Not a Primary Mechanism for Plasmon-Driven Photocatalysis. *ACS Nano* **2018**, *12*, 5848–5855.
- (75) Meng, Q.; Zhang, J.; Zhang, Y.; Chu, W.; Mao, W.; Zhang, Y.; Yang, J.; Luo, Y.; Dong, Z.; Hou, J. G. Local heating and Raman thermometry in a single molecule. *Sci. Adv.* **2024**, *10*, No. ead11015.
- (76) Anderson, P. W. Localized Magnetic States in Metals. *Phys. Rev.* **1961**, *124*, 41.
- (77) News, D. M. Self-Consistent Model of Hydrogen Chemisorption. *Phys. Rev.* **1969**, *178*, 1123.
- (78) Stefancu, A.; Halas, N. J.; Nordlander, P.; Cortés, E. Electronic excitations at the plasmon–molecule interface. *Nat. Phys.* **2024**, *20*, 1065–1077.
- (79) Avanesian, T.; Christopher, P. Adsorbate Specificity in Hot Electron Driven Photochemistry on Catalytic Metal Surfaces. *J. Phys. Chem. C* **2014**, *118*, 28017–28031.
- (80) Schirato, A.; Sanders, S. K.; Proietti Zaccaria, R.; Nordlander, P.; Della Valle, G.; Alabastri, A. Quantifying Ultrafast Energy Transfer from Plasmonic Hot Carriers for Pulsed Photocatalysis on Nanostructures. *ACS Nano* **2024**, *18*, 18933–18947.
- (81) Menzel, D.; Gomer, R. Desorption from Metal Surfaces by Low-Energy Electrons. *J. Chem. Phys.* **1964**, *41*, 3311.
- (82) Redhead, P. A. INTERACTION OF SLOW ELECTRONS WITH CHEMISORBED OXYGEN. *Can. J. Phys.* **1964**, *42*, 886–905.
- (83) Misewich, J. A.; Heinz, T. F.; News, D. M. Desorption induced by multiple electronic transitions. *Phys. Rev. Lett.* **1992**, *68*, 3737.
- (84) Olsen, T.; Gavnholt, J.; Schiøtz, J. Hot-electron-mediated desorption rates calculated from excited-state potential energy surfaces. *Phys. Rev. B* **2009**, *79*, No. 035403.
- (85) Persson, B. N. J.; Persson, M. Vibrational lifetime for CO adsorbed on Cu(100). *Solid State Commun.* **1980**, *36*, 175–179.
- (86) Gadzuk, J. W. Inelastic resonance scattering, tunneling, and desorption. *Phys. Rev. B* **1991**, *44*, 13466.
- (87) Gao, S. Quantum kinetic theory of vibrational heating and bond breaking by hot electrons. *Phys. Rev. B* **1997**, *55*, 1876.
- (88) Gao, S.; Lundqvist, B. I.; Ho, W. Hot-electron-induced vibrational heating at surface: importance of a quantum-mechanical description. *Surf. Sci.* **1995**, *341*, L1031–L1036.
- (89) Gao, S.; Busch, D. G.; Ho, W. Femtosecond dynamics of electron-vibrational heating and desorption. *Surf. Sci.* **1995**, *344*, L1252–L1258.
- (90) Gao, S.; Persson, M.; Lundqvist, B. I. Theory of atom transfer with a scanning tunneling microscope. *Phys. Rev. B* **1997**, *55*, 4825.
- (91) Gao, S. Heating and breaking of ad-molecule bond by inelastic tunneling. *Surf. Sci.* **1994**, *313*, 448–458.
- (92) Stipe, B. C.; Rezaei, M. A.; Ho, W.; Gao, S.; Persson, M.; Lundqvist, B. I. Single-Molecule Dissociation by Tunneling Electrons. *Phys. Rev. Lett.* **1997**, *78*, 4410.
- (93) Link, S.; Burda, C.; Wang, Z. L.; El-Sayed, M. A. Electron dynamics in gold and silver alloy nanoparticles: The influence of a nonequilibrium electron distribution and the size dependence of the electron–phonon relaxation. *J. Chem. Phys.* **1999**, *111*, 1255.
- (94) Voisin, C.; Christofilos, D.; Del Fatti, N.; Vallée, F.; Prével, B.; Cottancin, E.; Lermé, J.; Pellarin, M.; Broyer, M. Size-Dependent Electron-Electron Interactions in Metal Nanoparticles. *Phys. Rev. Lett.* **2000**, *85*, 2200.
- (95) Bigot, J. Y.; Merle, J. Y.; Cregut, O.; Daunois, A. Electron Dynamics in Copper Metallic Nanoparticles Probed with Femtosecond Optical Pulses. *Phys. Rev. Lett.* **1995**, *75*, 4702.
- (96) Arbouet, A.; Voisin, C.; Christofilos, D.; Langot, P.; Fatti, N. D.; Vallée, F.; Lermé, J.; Celep, G.; Cottancin, E.; Gaudry, M.; et al. Electron-Phonon Scattering in Metal Clusters. *Phys. Rev. Lett.* **2003**, *90*, No. 177401.
- (97) Iachello, F.; Ibrahim, M. Analytic and Algebraic Evaluation of Franck-Condon Overlap Integrals. *J. Phys. Chem. A* **1998**, *102*, 9427–9432.
- (98) Busch, D. G.; Ho, W. Direct Observation of the Crossover from Single to Multiple Excitations in Femtosecond Surface Photochemistry. *Phys. Rev. Lett.* **1996**, *77*, 1338.
- (99) Vattuone, L.; Gambardella, P.; Valbusa, U.; Rocca, M. HREELS study of molecular chemisorption on Ag(001). *Surf. Sci.* **1997**, *377*, 379, 671.
- (100) Messerli, S.; Schintke, S.; Morgenstern, K.; Nieminen, J.; Schneider, W.-D. Oxygen molecules on Ag(001): superstructure,

binding site and molecular orientation. *Chem. Phys. Lett.* **2000**, 328, 330.

(101) Hahn, J. R.; Ho, W. Chemisorption and dissociation of single oxygen molecules on Ag(110). *J. Chem. Phys.* **2005**, 123, 214702.

(102) Persson, B. N. J. Polarizability of small spherical metal particles: influence of the matrix environment. *Surf. Sci.* **1993**, 281, 153–162.

(103) Foerster, B.; Joplin, A.; Kaefer, K.; Celiksoy, S.; Link, S.; Sönnichsen, C. Chemical Interface Damping Depends on Electrons Reaching the Surface. *ACS Nano* **2017**, 11, 2886–2893.

(104) Foerster, B.; Spata, V. A.; Carter, E. A.; Sönnichsen, C.; Link, S. Plasmon damping depends on the chemical nature of the nanoparticle interface. *Sci. Adv.* **2019**, 5, No. eaav0704.

(105) Therrien, A. J.; Kale, M. J.; Yuan, L.; Zhang, C.; Halas, N. J.; Christopher, P. Impact of chemical interface damping on surface plasmon dephasing. *Faraday Discuss.* **2019**, 214, 59–72.

(106) Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, 6, 4370.

(107) Kazuma, E.; Lee, M.; Jung, J.; Trenary, M.; Kim, Y. Single-Molecule Study of a Plasmon-Induced Reaction for a Strongly Chemisorbed Molecule. *Angew. Chem., Int. Ed.* **2020**, 59, 7960–7966.

(108) Kazuma, E.; Lee, M.; Jung, J.; Trenary, M.; Kim, Y. Real-Space Observations of Multiple Reaction Pathways Enabled by Plasmonic Hot Carriers. *J. Phys. Chem. C* **2023**, 127, 10953–10959.

(109) Halas, N. J.; Lal, S.; Chang, W.-S.; Link, S.; Nordlander, P. Plasmons in Strongly Coupled Metallic Nanostructures. *Chem. Rev.* **2011**, 111, 3913.