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Phonon-mediated ultrafast dynamics in self-assembled monolayers of 4-mercaptobenzoic acid on gold

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Non-equilibrium interactions between plasmonic metals and adsorbed molecules lie at the heart of emerging applications such as plasmonic photocatalysis and sensing, though the ultrafast charge and energy transfer mechanisms arising from these interactions are not well understood. Herein, we investigate the ultrafast dynamics of Au nano-islands tethered with a self-assembled monolayer (SAM) of electron-withdrawing 4-mercaptobenzoic acid (4MBA) molecules. Ultrafast UV-visible transient absorption spectroscopy following excitation of the interband transition in Au reveals three well-known, characteristic time constants that quantify electron-electron (el-el), electron-phonon (el-ph) and phonon-phonon (ph-ph) scattering lifetimes. When comparing the dynamics of bare Au and 4MBA-Au, we find that the el-ph and ph-ph scattering lifetimes are notably longer in 4MBA-Au. Density functional perturbation theory calculations ascribe the elongation in el-ph lifetimes in 4MBA-Au to the significant coupling of acoustic phonon modes of Au with certain molecular vibrations of 4MBA, leading to decreased spatial overlap between carrier electronic states and the acoustic modes. We speculate that the elongation of ph-ph scattering lifetimes in 4MBA-Au arises due to poor thermal conductivity of the SAM which disrupts efficient energy dissipation from Au to the environment, thus slowing down the thermalization of phonons. This work provides a glimpse into how molecular adsorbates modify the charge carrier and phonon dynamics of Au and sets the stage for further systematic exploration of plasmonic metal-molecule interactions.

Introduction

Plasmonic nanomaterials play a central role in emerging areas such as plasmonic photocatalysis^{1–4}, novel photovoltaic devices^{5–7}, photothermal cancer therapies^{8,9}, and sensing^{9–11}, where unique nanoscale light-matter interactions can elicit targeted transformations at the molecular scale. For example, in plasmonic photocatalysis, excitation of the localized surface plasmon resonance (LSPR) or interband transitions of the plasmonic metal has been shown to effect chemical transformations ranging from oxidation/reduction^{12–14}, cross-coupling^{15–17}, desorption^{18–20}, isomerization^{21,22} and polymerization^{23–25}, with a high degree of selectivity, although the role of "hot" charge carriers vs. photothermal heating effects is heavily debated.²⁶ These applications critically rely on the interactions between plasmonic metals and molecular adsorbates^{3,27–29}, which are thought to involve charge transfer (CT) and/or energy transfer (ET) pro-

cesses between the metal and the molecule that time scales from a few femtoseconds to nanoseconds. Whereas a large body of steady-state investigations exists, for example on the outcomes of plasmon-enhanced photocatalytic reactions^{1,30}, there is limited work exploring real-time non-equilibrium dynamics in controlled, model systems essential for a bottom-up understanding of plasmonic metal-molecule interactions.³¹

To set the stage for understanding plasmonic metal-molecule interactions, we first consider the dynamics in pristine plasmonic metals. Absorption of a photon by a plasmonic metal nanostructure can excite 1) a LSPR, which is characterized by the collective, coherent oscillations of electrons in the conduction band that decay via Landau damping within tens of femtoseconds to generate electrons (holes) above (below) the Fermi energy (E_F)^{32–34}, within the sp band, and/or 2) an interband transition that promotes an electron from below E_F to above E_F , generating electrons and holes in the hybridized sp and d bands³⁵, respectively. Both excitation regimes initially generate non-thermalized charge carriers that relax to a Fermi distribution via electron-electron (el-el) scattering within hundreds of femtoseconds.^{36,37} These charge carriers further relax via scattering with acoustic phonons on timescales < 10 ps^{38,39}, and the resulting hot phonon distri-

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bution eventually equilibrates via phonon-phonon (ph-ph) scattering with the surrounding environment on > 100 ps time scales, generating a thermalized distribution of phonons.^{37,38}

Various mechanisms have been proposed to attempt to explain the manner in which dynamics in a pristine metal changes when new CT and ET pathways arise from plasmonic metal-molecule interfaces, although systematic real-time observations of these processes have been rather limited. LSPR excitation can be followed by indirect CT, where plasmons first decay to form "hot" charge carriers in the metal that then transfer to the molecular orbitals of the adsorbate.⁴⁰ Direct CT is proposed to occur in systems with strong hybridization between the metal and adsorbate states, where the dephasing of LSPR leads to a direct electronic transition between hybrid metal-molecule states.^{12,41} Alternatively, an interband excitation can lead to abstraction of electrons and/or holes from the metal by the adsorbate molecule.⁴² ET, on the other hand, results in photothermal heating of the adsorbate, which can also drive chemical transformations. This mechanism is preceded by el-el or el-ph scattering mechanisms that take place on femtosecond to picosecond timescales. Interestingly, LSPR and interband excitations have been shown to elicit different reaction outcomes, with initial electron or hole transfer from the metal to the adsorbate being postulated as the cause.^{43,44}

There are relatively few ultrafast investigations that have explicitly explored plasmonic metal-molecule interactions, with the majority of these studies done in the solution phase where solvent molecules can obscure detailed insights on these interactions.^{45–51} These studies reveal that surface-bound molecules on plasmonic metals can profoundly influence ultrafast relaxation processes and herein we summarize the salient results of a few selected works. One of the seminal works that studied metal-molecule interactions was by El Sayed and co workers using ultrafast UV-visible transient absorption spectroscopy (TAS) of thiolated DNA ligands on Au nanoparticles.⁴⁷ This work uncovered faster relaxation in time regimes of < 10 ps upon LSPR excitation of thiolated DNA-bound Au nanoparticles compared to unthiolated nanoparticles, as a result of adsorbate desorption generating an additional pathway for energy dissipation. This study showed that exposure to ultrafast pulses may cause adsorbate desorption due to the coupling between excited electrons and surface Au-S vibrations and not due to conventional heating as a result of ph-ph relaxation that typically occurs on time scales > 100 ps. In another study, LSPR excitation of 70 nm Au nanoparticles capped with 4-nitrobenzenethiol and 4,4'-dimercaptoazobenzene ligands, probed with transient surface-enhanced Raman spectroscopy, indicated charge delocalization on time scales of < 5 ps, which was attributed to the electronic wave function of the plasmonic metal spreading over nearby adsorbates or solvent molecules.⁴⁸ A time-resolved surface-enhanced impulsive stimulated Raman spectroscopy study on Au nanoparticle assemblies tethered with trans-1,2-bis(4-pyridyl)ethylene provided evidence that the Au-adsorbate bond weakens and the adsorbate molecules migrate away from hot spots with a lifetime of 3.3 ps.⁴⁹ Shabaninezhad et al. studied the influence of the adsorbate on LSPR-excited Au clusters using TAS and found that el-ph coupling strength is smaller in the presence of aromatic adsorbates com-

pared to aliphatic adsorbates.⁵⁰ To the best of our knowledge, the only ultrafast study on non-solvated Au-adsorbate systems investigated how a SAM of 4-methoxy thiophenol affects the carrier dynamics upon plasmonic excitation of Au.⁵² This study showed that tethering the adsorbate to a Au/semiconductor (TiO_2) system mediates charge carrier recombination. However, the incorporation of the TiO_2 layer adds more complexity, further highlighting the need for better understanding of non-adiabatic dynamics of Au-adsorbate systems.

Knowledge of how the two modes of electronic excitation and variations in the electronic properties of the molecules result in different outcomes^{44,53,54} requires that we first understand the ultrafast processes contributing to CT and ET pathways. However, the potential coexistence of multiple mechanisms on overlapping time scales, short carrier lifetimes, variations stemming from nanoscale morphology, and challenges to theoretical treatments of these interactions have posed significant obstacles. Overcoming these obstacles requires a systematic, bottom-up approach of understanding ultrafast dynamics in model systems as a controllable starting point. As a well-defined model system without complicating solvent influences, herein we report our investigations of the dynamics of thin Au nano-islands with self-assembled monolayers (SAM) of the electron-withdrawing 4-mercaptobenzoic acid (4MBA) molecules following interband excitation—an excitation mode that is relatively less explored. Our joint experimental and theoretical study characterizes and compares steady-state and ultrafast dynamics of Au and 4MBA-Au systems, revealing a marked slowdown in the thermalization of charge carrier and phonon populations in the presence of 4MBA. Theory calculations provide insights into the observed changes indicating that strong coupling between acoustic phonon modes of Au and certain vibrational modes of 4MBA may increase scattering lifetimes.

Experimental and Theoretical Methods

Sample Preparation

A discontinuous gold film was prepared by sputtering Au onto a 1 mm thick $\text{CaF}_2(111)$ window using a K550X plasma sputter coater (Quorum Technologies) at 50 mA for 10 seconds with continuous Ar gas flow to create Au films of approximately 4 nm thickness. Two samples were deposited at the same time to ensure that the thickness of Au and the optical properties are identical, as confirmed by our steady-state spectroscopic characterization. A self-assembled monolayer (SAM) of 4MBA was prepared by incubating one of the two simultaneously deposited Au samples in a 3 mM 4MBA solution in ethanol for 48 hours, followed by multiple washing cycles with ethanol and deionized water. This is a well-established procedure known to form SAMs on Au.^{55–57} The Au sample tethered with 4MBA will be referenced as 4MBA-Au henceforth.

Steady-State Characterization

The static UV-visible spectra of the Au and 4MBA-Au samples were measured soon after Au deposition and 4MBA tethering using a Perkin Elmer Lambda 1050+ spectrometer. A CaF_2 sub-

strate was used as the background, which is subtracted from the UV-visible spectrum of the sample. The vibrational modes of the SAMs were characterized using a Burkert Tensor 27 Fourier Transform Infrared (FTIR) spectrometer, which was purged with N₂ for 15 minutes before measurements to minimize background contributions from ambient H₂O and CO₂. FTIR and static UV-visible spectra were taken before and after laser irradiation to ensure the stability of 4MBA molecules and Au, respectively. The surface morphology of Au was characterized using the Elstar FEG electron column of a FEI Helios NanoLab 660 dual beam FIB Scanning Electron Microscope (SEM). Crystallographic information of Au was obtained using PANalytical EmpyreanTM X-ray diffractometer (XRD).

Transient UV-visible Absorption Spectroscopy

A home-built setup was used to carry out the UV-visible TAS described here. The 800 nm, 1.5 mJ, 1 kHz, 35 fs output of a regenerative amplifier (Coherent Legend Elite Duo) was split in a 80:20 ratio for generating the pump and the probe, respectively. For the probe arm, the fundamental is focused into a 2 mm thick CaF₂(001) single crystal window to generate a white light continuum (WLC) spanning 375 nm to 730 nm, which is then collimated by an Al parabolic mirror. The fundamental 800 nm and the WLC are *p*-polarized light pulses. A dichroic beam splitter filters out the fundamental 800 nm, transmitting just the WLC. The beam is then focused by another Al parabolic mirror to a 190 μ m ($1/e^2$) diameter spot, reaching the sample plane normal to the sample surface. The transmitted probe is collimated using an achromatic lens and sent to a spectrometer (Avantes) with a detection range of 250 to 820 nm. For the pump arm, the fundamental 800 nm beam was chopped at 500 Hz, sent through a half waveplate and a linear polarizer, then onto a Ag retro-reflector mounted on a motorized stage that controls the delay between the pump and the probe from -2 ps to 1.4 ns, and finally to a BBO crystal (BBO-603H, Eksma Optics) to generate the *s*-polarized 400 nm via second harmonic generation. The pump is focused to a 270 μ m ($1/e^2$) diameter spot and reaches the sample plane at a $\sim 10^\circ$ angle with respect to the surface normal. Both the pump and the probe intersect the sample at their respective focal points, and the sample is mounted on a stage that rasters vertically and horizontally along the plane of the sample during measurements to avoid damage. At each time delay, we measure the differential absorption given by

$$\Delta mOD = -\log\left(\frac{I_{pump,on}}{I_{pump,off}}\right) \times 10^3 \quad (1)$$

where $I_{pump,on}$ is the probe intensity with pump illumination and $I_{pump,off}$ is the probe intensity with the pump blocked.

The $1/e^2$ width of the instrument response function (IRF) was determined as 223 ± 17 fs by fitting the rise of the induced absorption (centered at 550 nm) of a ZnSe crystal near time-zero. The WLC has an inherent chirp, which shifts the experimental time-zero as a function of probe wavelength; the following procedure was used to correct the chirp prior to fitting the data. First, the temporal location of the maximum transient signal is identi-

fied as a function of wavelength between 410-620 nm. Then the temporal position of this signal maximum as a function of wavelength is fitted to a third order polynomial, and the experimental time axis at each wavelength is shifted such that the position obtained from the fit is set to time-zero. Global fit analysis was performed on chirp-corrected TAS in the range of 410-730 nm using the Glotaran 1.5.1 software package⁵⁸.

Computational Details

We computed the projected density of states (PDOS) using the Vienna *Ab initio* Simulation Package (VASP).^{59,60} Electronic exchange–correlation effects were treated within the generalized-gradient approximation using the Perdew–Burke–Ernzerhof (PBE) functional. The Brillouin zone was sampled with a Γ -centered Monkhorst–Pack *k*-point mesh of $9 \times 4 \times 1$, and a plane-wave kinetic-energy cutoff of 500 eV was applied. PDOS calculations were performed for pristine Au(111), an isolated 4MBA molecule, and the 4MBA–Au interface. The pristine Au model uses a $5.12 \times 11.8 \times 29.63$ Å supercell with ~ 7 Å of vacuum along the *z* direction and contains 40 Au atoms. The isolated 4MBA molecule is placed in a $5.12 \times 11.8 \times 10$ Å supercell. For the 4MBA–Au model, the supercell size is identical to that of pristine Au, with two 4MBA molecules per unit cell adsorbed on the Au surface with their sulfur ends toward the surface and their opposite ends oriented toward the vacuum⁶¹. Additional computational details are provided in section S2 of the SI.

Results and Discussion

Experimental Characterization of Steady-State Au and 4MBA–Au

To circumvent solvation effects and contributions from capping ligands that can influence the ultrafast dynamics of solution-phase colloidal nanoparticles, our samples are a discontinuous thin film of Au with a SAM of 4MBA, which enables us to exclusively study the plasmonic metal-molecule interactions. The SEM image of an example Au sample in Figure 1A shows a discontinuous gold film with nano-island like structure. The PXRD (Figure 1B) reveals the presence of CaF₂(111), Au(111) and Au(200) planes. Of these, the Au(111) plane is the most abundant phase in the sample with only a minor presence of the Au(200) phase. The static UV-visible absorption spectra of the two Au samples that were deposited together under identical conditions are displayed in Figure 1C (solid blue line and dashed red line), showing identical optical absorption lineshapes. The sample thickness was estimated to be ~ 4 nm, by comparing the measured UV-visible spectrum with a study that measured the transmission spectra of Au at different thicknesses.⁶² The broad and intense feature centered at ~ 700 nm is attributed to the LSPR. At wavelengths shorter than 500 nm, a feature attributed to the interband transition ($5d \rightarrow 6sp$) is observed.

In small Au nanoparticles, the LSPR and interband excitation regions often overlap, making it difficult to distinguish the dynamics that stem from these two regimes of excitation.^{63,64} In our samples, the ~ 4 nm thick nano-island like discontinuous Au film circumvents this issue and provides well-separated interband

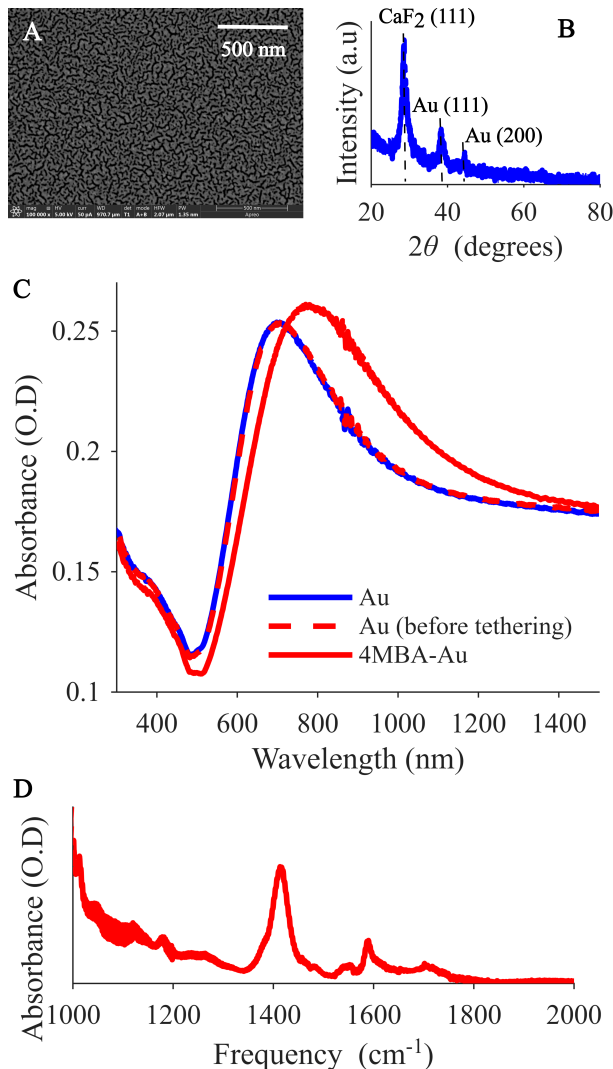


Fig. 1 A) SEM image and B) PXRD pattern of a bare Au sample. C) Static UV-visible spectra of bare Au (blue and dash red line) and of 4MBA-Au (red solid line) after tethering 4MBA to the bare Au sample represented by the dashed red line. D) FTIR spectrum of 4MBA-Au.

and plasmonic excitation regions.

Upon SAM deposition, 4MBA is chemisorbed onto the Au surface via a strong Au-S bond. The optical absorption spectrum of 4MBA-Au is displayed as a solid red line in Figure 1C. A clear redshift and broadening of the LSPR feature is observed upon SAM formation. Previous studies have attributed the broadening to chemical interface damping^{65,66}, and the redshift is attributed to changes in the dielectric constant and/or to the decrease in the free electron density of Au as a result of binding with thiol molecules^{47,65,67,68}, although the extent of these changes in our sample could also stem from thin-film inhomogeneities. The tethering of 4MBA leaves the wavelength region corresponding to interband transitions largely unchanged.

Figure 1D shows the FTIR spectrum of 4MBA-Au, confirming the presence of 4MBA on the surface. After Fano line shape correction⁶⁹, these spectra reveal three distinct vibrations at ~ 1415 , ~ 1590 and ~ 1710 cm^{-1} , in agreement with previous infrared/Raman measurements of 4MBA SAM on Au^{56,70,71}; the

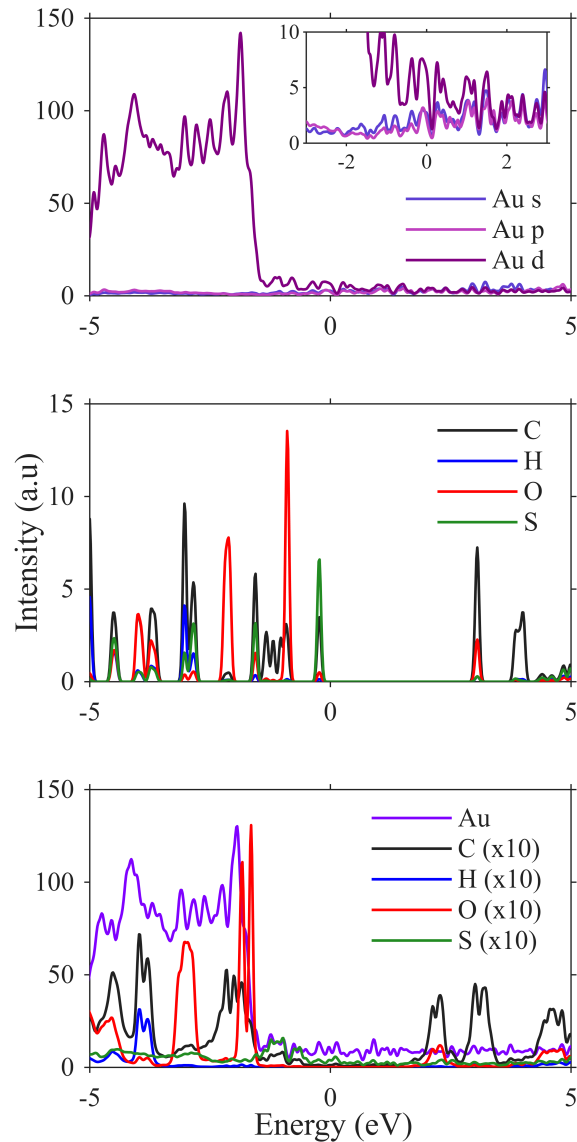


Fig. 2 PDOS of A) pristine Au, b) isolated 4MBA molecule, and C) 4MBA-Au obtained using DFT calculations. Energy axis has been shifted so that E_F is at 0 eV for each system.

features are assigned to the O=C-OH symmetric stretching vibration, the C=C stretch vibration of the aromatic ring, and the C=O stretch vibration, respectively.

Electronic Structure Calculations of Ground-State Au and 4MBA-Au

Partial density of states (pDOS) near E_F for Au, isolated 4MBA, and 4MBA-Au systems, obtained by ground state DFT calculations, are shown in Fig. 2A, B and C, respectively. The pDOS of the pristine Au slab (2A) has main contributions from s/p bands above E_F , and from d bands below E_F , in agreement with previously reported electronic structure calculations of Au films/nanoparticles/metal clusters⁷²⁻⁷⁴. These studies further show that s and p orbitals with principle quantum number 6 and d orbitals with principle quantum number 5 mainly contribute to the pDOS around E_F .

Fig. 2B presents the pDOS of an isolated 4MBA molecule where the highest occupied molecular orbital (HOMO) mainly has sulfur character, while the lowest unoccupied molecular orbital (LUMO) has both carbon and oxygen character. Indeed, as shown in Fig. S1, the LUMO is delocalized on the $-\text{COOH}$ moiety and the aromatic ring, while the HOMO is localized around the sulfur atom. For the combined system of 4MBA-Au, the pDOS show particularly strong hybridization of the HOMO with Au bands, while the LUMO hybridizes with the Au states to a lesser extent (Figure 2C). This is supported by orbital plots of the HOMO and LUMO states in the combined 4MBA-Au system (Fig. S2).

Our calculations return a HOMO-LUMO gap of 3.25 eV in isolated 4MBA, which underestimates the experimentally measured HOMO-LUMO gap of 4.46 eV in the liquid phase ($\text{pH} = 5.02$)⁷⁵. The HOMO-LUMO gaps are expected to be modified by improved treatments such as the GW approximation of electronic correlations effects, which are underestimated at the DFT-PBE level employed in our study. Nevertheless, scanning tunneling spectroscopy studies carried out on 4MBA-Au show that the experimental HOMO and LUMO qualitatively agree with our pDOS, and that the broadening of sulfur molecular orbital contributions closer to E_F is indicative of strong hybridization between 4MBA and Au surface states.⁷⁶

Ultrafast Dynamics of Au and 4MBA-Au

To investigate how 4MBA molecules alter the dynamics of pristine Au, we performed ultrafast UV-visible TAS on Au and 4MBA-Au following interband excitation at 400 nm. The 400 nm pump fluence was set to $50 \mu\text{J cm}^{-2}$, which we established using FTIR and UV-visible spectroscopies to be below the threshold for sample damage (Section S3 in the SI). Furthermore, this fluence is ~ 40 times smaller compared to the threshold fluence used in an experiment to study photoinduced desorption in thiolated DNA-Au nanoparticles.⁴⁷

The falsecolor maps in Figures 3A and B present the transient absorption (TA) spectra from -1 to 10 ps time delays for Au and 4MBA-Au, respectively. We only display probe wavelengths from 410-730 nm as intense pump scatter is present near 400 nm, while the poor signal to noise ratio arising from low white light intensity for $\lambda > 730$ nm dictates the long wavelength cutoff. The TA spectra of bare Au consist of a positive (induced) absorption feature centered around 500 nm and negative absorption (bleach) features that flank the positive feature on both sides. Similar features for ultra-thin Au films have been previously reported.^{63,77,78} The 400 nm interband excitation generates holes and electrons in the $5d$ and $6sp$ bands, respectively, as described above. The tail of a bleach feature at $\lambda < 430$ nm can be attributed to a ground state bleach (GSB) due to the reduction in the $5d \rightarrow 6sp$ absorption following interband excitation. The positive feature centered around 500 nm corresponds to excited state absorption (ESA) from transitions that fill the photogenerated holes from states deeper below E_F . The negative feature at $\lambda > 610$ nm arises from changes in the LSPR upon photoexcitation, as deduced from the expression for the plasmon resonance frequency (ω_p) from the Drude model and Mie Theory, ω_p

$= \sqrt{ne^2 / \epsilon_0 m^* (\epsilon_\infty + 2\epsilon_m)}$, where n is the density of free electrons, e is the electronic charge, m^* is the effective mass of the electron, ϵ_m is the dielectric constant of the medium, ϵ_∞ is the high-frequency dielectric constant of Au due to interband transitions, and ϵ_0 is the vacuum dielectric constant.⁴⁷ Interband transitions increase the free electron density causing the LSPR frequency to blueshift.⁶³ Increased lattice temperature due to el-ph scattering modifies the dielectric constant, which in turn broadens the LSPR band.^{63,79} The combination of these two factors is reflected in the TA spectra as a negative differential adsorption at $\lambda > 610$ nm. The narrowing of the ESA and GSB features and the decay in signal intensity with time delay reflects the relaxation of charge carriers. Similarly, the bleach at $\lambda > 610$ nm recovers as the electronic temperature cools.

Although the salient transient spectral features in both Au and 4MBA-Au are similar, marked differences are observed in the ultrafast relaxation times of the two samples. According to established models, interband excitation creates a non-Fermi charge carrier distribution, which subsequently equilibrates to a Fermi distribution via el-el scattering. The thermalized charge carriers lose their energy to the lattice via el-ph scattering, thus increasing the lattice temperature, and the lattice phonons eventually reach equilibrium with the surrounding environment via ph-ph scattering. We note here that we use the terms el-el and el-ph to describe both electron and hole charge carrier interactions, consistent with terminology commonly used in the field. While there is a clear timescale separation between these processes, we note that they are not strictly sequential in nature.^{77,78,80} Herein, we choose a three-component (tri-exponential) kinetic model^{81,82} to fit the experimental data out to our longest time delay of 1.4 ns. We carried out global target analysis using the Glotaran software⁵⁸, in which identical time constants were enforced across all wavelengths while allowing the amplitudes to vary spectrally. We begin with this approach to obtain an averaged description of the dynamics. The extracted lifetimes and standard errors for each time constant are shown in Table 1. More details on the fitting procedure can be found in section S5 of the SI.

Table 1 Decay lifetimes of charge and energy carriers of Au and 4MBA-Au obtained via a global fit analysis. Error bars are the standard error obtained by independently fitting multiple measurements performed under identical conditions.

System	τ_{el-el} (fs)	τ_{el-ph} (fs)	τ_{ph-ph} (ps)
Au	269.60 ± 4.41	859.92 ± 26.41	144.32 ± 15.30
4MBA-Au	246.40 ± 8.86	1032.85 ± 32.56	278.36 ± 99.29

The first time constant (τ_{el-el}) from our fits represents the lifetimes of non-thermalized charge carriers and we find no significant difference between 4MBA-Au and Au, although the fidelity with which we can quantify this time constant and extract any differences is compromised by limitations imposed by our IRF. The second (τ_{el-ph}) and third (τ_{ph-ph}) time constants obtained from the global analysis represent the lifetimes of thermalized electrons and non-thermalized phonons, respectively. We consistently find that these lifetimes are longer in 4MBA-Au compared to bare Au, as shown in Table 1, suggesting that the picosecond

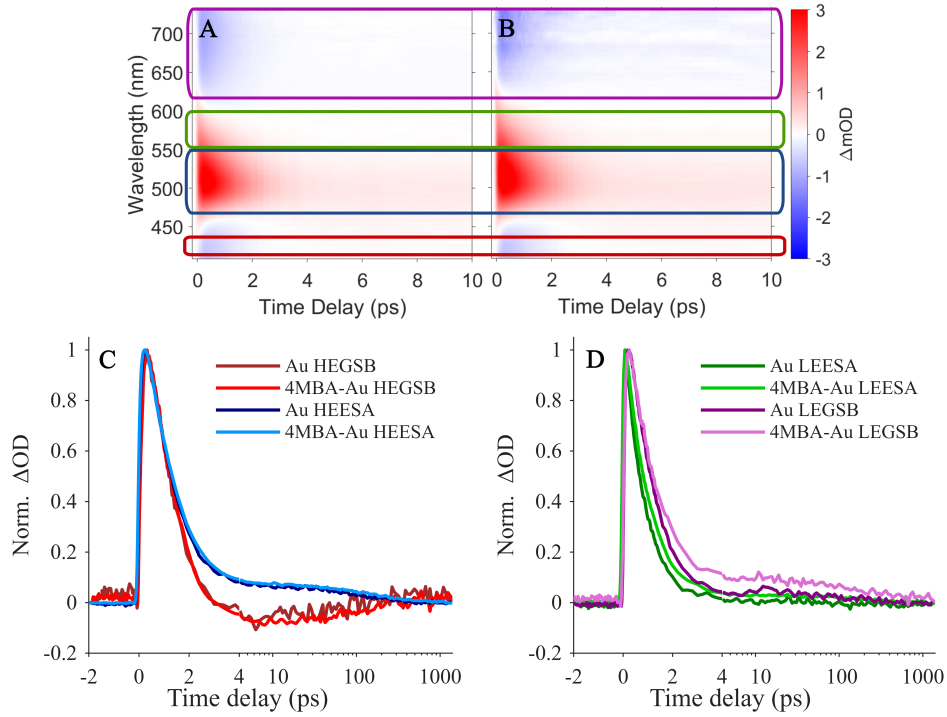


Fig. 3 TA signal for A) Au and B) 4MBA-Au upon 400 nm interband excitation. The spectral regions highlighted by red, blue, green, and purple represents HEGSB, HEESA, LEESA and LEGSB, respectively. Averaged and normalized TA signal of C) HEGSB and HEESA and D) LEESA and LEGSB. The darker shades represent the signal from Au and the lighter shade represents the signal from 4MBA-Au. The time delay axis follows a linear scale upto 4 ps and is logarithmic afterwards.

and hundreds of picosecond dynamics are indeed influenced by the 4MBA SAM.

Whereas global target analysis provides a robust means to assess general trends by reducing parameter correlations, it does not capture wavelength dependent variations arising from different physical processes. To qualitatively assess the differences in the picosecond and hundreds of picosecond dynamics between Au and 4MBA-Au, we first explore the coarse probe wavelength dependence across four wavelength regions, noting that multiple processes may contribute to the dynamics within each region: 1) 410-430 nm (high energy ground state bleach, HEGSB), 2) 470-550 nm (high energy excited state absorption, HEESA), 3) 550-600 nm (low energy excited state absorption, LEESA), and 4) 610-730 nm (low energy ground state bleach, LEGSB); the spectral regions are highlighted in red, blue, green, and purple in Figure 3A and B, respectively. We find that both high energy features decay at similar rates for 4MBA-Au and Au systems. However, the low energy/long wavelength transient signals decay faster in Au compared to 4MBA-Au; these differences are clearly seen in the time regimes ranging from a few picoseconds to hundreds of picoseconds. We carried out identical TAS experiments with different pairs of Au and 4MBA-Au samples and obtained similar trends (see SI section S4). The wavelength-dependent differences in decay rates suggest that a subset of charge carriers, i.e., those that are probed at longer wavelengths, are particularly sensitive to the metal-molecule interface.

In the following discussion, we examine the wavelength dependence of lifetimes in greater detail, with a particular emphasis on

the ESA feature, starting with the case of bare Au. As described above, experimental constraints limit our probe wavelength range to capture only the tails of the two bleach features, and we find no probe wavelength dependence to the decay rates in the HEGSB. By contrast, the ESA feature shows a discernible wavelength dependence, where the decay of the TA signal slows down with increasing probe wavelength from ~ 470 to 500 nm, and becomes faster going from ~ 500 to 600 nm. Figure 4 shows the probe wavelength dependent τ_{el-ph} for Au and 4MBA-Au, calculated by averaging in 2-nm windows across the ESA feature and fitting each window to a three-component decay model. The interband transition threshold (ITT) energy in Au is ~ 2.4 eV (517 nm),⁷⁸ and thus the 3.1 eV (400 nm) pump can excite electrons from the 5d band to states above the E_F . Following this excitation, the initially photogenerated holes in the 5d band relax towards the E_F within tens of femtoseconds^{83,84}, and the subsequent probe interaction acts to fill these holes by promoting electrons from the 5d band, resulting in an induced absorption, as shown in Figure 5. Due to the large width of the 5d band (Figure 2), the holes can be monitored across a broad swath of probe photon energies both above and below the ITT (Figure 5). Probe photon energies less than the ITT promote electrons near the top of the 5d band to fill the holes close to the E_F , while probe photon energies greater than the ITT can also promote electrons deeper in the 5d band to fill photogenerated holes near the E_F . In addition, probe photon energies greater than the ITT can monitor photoexcited electrons above the E_F , resulting in a bleach (Figure 5, double-sided dashed arrow). We eliminate the possibility of the probe in-

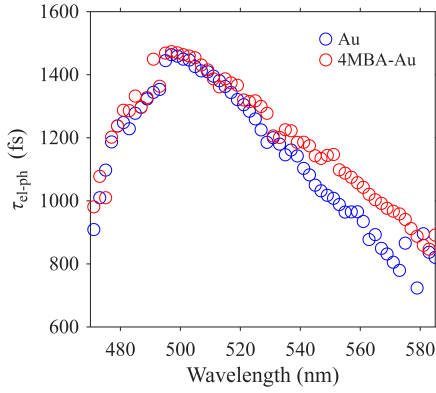


Fig. 4 τ_{el-ph} scattering lifetimes for Au (blue) and 4MBA-Au (red) obtained by averaging the TA spectra over 2 nm windows and fitting the time-resolved signal to a three-step kinetic model.

teraction further promoting photogenerated electrons above the E_F to higher lying states within the $6sp$ band based on previous DFT band structure calculations, which show that the intensity of transitions within the $6sp$ band is much weaker than transitions from the $5d$ to $6sp$ bands⁸⁵.

Therefore, probe energies above the ITT provide information on both photoexcited holes and electrons, giving rise to overlapping induced absorption and bleach contributions, while probe energies below the ITT only monitor holes via induced absorption transitions. Consequently, the ESA at $\lambda > \sim 517$ nm provides information exclusively on the hole dynamics^{77,86}, while signals between ~ 470 -517 nm contain information on both electron and hole dynamics, which are difficult to extricate due to overlapping spectral contributions. Hence, we focus on the LEESA region at probe wavelengths greater than 510 nm to understand hole dynamics in Au and how it is influenced by the chemisorbed 4MBA molecules.

Prior transient reflectivity studies^{77,78,86} of Au have revealed that higher energy holes are monitored with longer probe wavelengths, and vice versa (Figure 5). In both Au and 4MBA-Au, shorter probe wavelengths, which primarily probe low-energy holes closer to the E_F , exhibit longer τ_{el-ph} than longer probe wavelengths, which primarily probe the high-energy holes deeper below the E_F (Figure 4). Because τ_{el-ph} is proportional to $\sqrt{k_B T / E}$ where k_B is the Boltzmann constant, T is the lattice temperature, and E is the carrier energy,⁸⁷ these observations are in agreement with the predictions from this equation that higher energy carriers have shorter lifetimes. The primary channel for el-ph scattering occurs via energy transfer from holes to acoustic phonons of Au.⁸⁶ High energy charge carriers can excite phonons with a broader energy range, leading to a faster picosecond decay. The τ_{el-ph} is similar for Au and 4MBA-Au near 500 nm, but these values increasingly diverge as the probe wavelength increases from 500 to 600 nm, with bare Au exhibiting shorter τ_{el-ph} compared to 4MBA-Au at longer probe wavelengths. This implies that the presence of 4MBA slows down the el-ph scattering rates of primarily the energetic holes, as compared to bare Au.

To explain this marked increase in τ_{el-ph} in the presence of

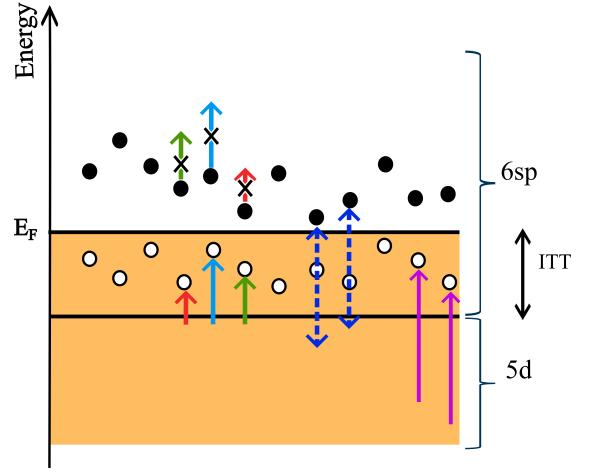


Fig. 5 Schematic of probe interactions with thermalized charge carriers in bare Au after interband excitation. One-sided arrows indicate charge carrier absorption and double-sided dashed arrows indicate GSB.

4MBA, we seek to develop a conceptual picture of how the el-ph scattering rate is influenced by the molecule. For this, we draw from the Fermi's Golden Rule expression for carrier-phonon scattering rates, although due to the prohibitive computational cost of explicitly calculating the terms in the expression, we limit this discussion to the qualitative insights gained from vibrational coupling analysis as described in section S2 of the SI. The state-to-state form of the Fermi's Golden Rule scattering rate between initial (i) and final (f) carrier states in Au is given by $\tau_{el-ph}^{-1}(i \rightarrow f) = (2\pi/\hbar) |\langle i | H_{el-ph} | f \rangle|^2 \delta(E_f - E_i - \hbar\omega_q)$, for Au acoustic phonons of energy $\hbar\omega_q$ in resonance with the energy difference between final and initial carrier states $E_f - E_i$. The magnitude of the electron-phonon coupling matrix element, $M^2 = |\langle i | H_{el-ph} | f \rangle|^2$, is dependent on the spatial distribution of the initial and final carrier states and of the phonon modes. Our calculations for the slab model of 4MBA-Au show that the Au acoustic phonon modes are strongly coupled to certain molecular vibrational modes (Figure S3 in the SI), causing significant delocalization of vibrations and yielding atomic displacements spanning Au and 4MBA. As a result, the spatial overlap between the acoustic modes with the carrier states is reduced in the presence of 4MBA, leading to a decrease in the magnitude of the el-ph coupling matrix element $M^2 = |\langle i | H_{el-ph} | f \rangle|^2$, and therefore extending the el-ph scattering lifetime in 4MBA-Au relative to bare Au. To explain the trends in the wavelength dependence of el-ph scattering times (Fig. 4), we consider the relaxation rate of an initial state (i) to a continuum of final states by summing over all final states, $\tau_{el-ph}^{-1}(i) = \sum_f \tau_{el-ph}^{-1}(i \rightarrow f)$. Invoking the relaxation time approximation, $\tau_{el-ph}^{-1}(i) \approx \int dE \text{DOS}(E) M(E)^2$, the relaxation rate scales with the density of final states (DOS) that satisfies energy and momentum conservation, and with the magnitude of the matrix element, M . For holes in the $6sp$ band, the density of final states decreases with decreasing hole energy, eventually reaching zero at the Fermi level (as Γ -point acoustic phonons have zero density of states). We therefore deduce that while the relaxation rates for all holes are reduced by the presence of 4MBA, this reduction is

largest for high energy holes and smallest for holes near the Fermi level (corresponding to 517 nm in Fig. 4).

Turning to the long, hundreds of picosecond dynamics characteristic of ph-ph scattering, Figure 3D shows weak transient absorption features even at time delays > 10 ps, which is past the lifetimes for charge carrier recombination in Au and 4MBA-Au. These weak transient signals at long time delays stem from changes in the lattice temperature that modify the dielectric constant⁸⁸, giving rise to a slightly different absorption profile compared to unexcited Au. Similar to τ_{el-ph} , we find that the τ_{ph-ph} lifetimes are extended in 4MBA-Au compared to pristine Au (Table 1 and Figure 3D). As theory calculations of ph-ph interactions in 4MBA-Au are computationally costly and outside of the scope of our current study, we speculate on a couple of possible causes that may give rise to this observation. A SAM does not change interatomic force constants deep in bulk of Au, but the formation of a new interface between Au and the surroundings could potentially alter the coupling between the Au acoustic phonons and the environment. Au-thiol adsorbates are known to form an interface with poor thermal conduction⁸⁹⁻⁹¹, where the SAM layer acts as a barrier that disrupts efficient energy dissipation from Au to the environment. In addition, the vibrational DOS of Au is continuous and broadband⁹², while the molecular vibrational DOS is discrete with narrow bands. This poor overlap in vibrational densities may also hinder efficient energy transport across the interface, thus elongating the ph-ph scattering lifetimes in 4MBA-Au compared to bare Au.^{89,93}

Conclusions

In summary, we investigated the influence of the electron-withdrawing 4-mercaptobenzoic acid self-assembled monolayers on the ultrafast dynamics of Au nanostructures using a combination of steady-state characterization techniques, DFT calculations, and femtosecond transient absorption spectroscopy. Following 400 nm interband excitation, the el-ph and ph-ph scattering lifetimes are longer in 4MBA-Au than in pristine Au, indicating that the presence of 4MBA substantially prolongs the relaxation times of charge carriers and phonons. Wavelength-dependent analysis uncovers that high-energy holes are especially sensitive to 4MBA-Au interactions, exhibiting longer el-ph scattering lifetimes than in pristine Au. Density functional theory reveals that the prolonged τ_{el-ph} lifetimes arise from reduced el-ph scattering efficiency in 4MBA-Au due to significant coupling between the Au acoustic phonons and 4MBA molecular modes that delocalizes the vibrations across the interface and decreases spatial overlap with charge carrier states. Furthermore, the extended hundreds of picoseconds dynamics in 4MBA-Au indicates that 4MBA acts as a thermal barrier, impeding gold lattice cooling.

The combination of ultrafast spectroscopy and first-principles calculations presented herein reveal the manner in which Au-adsorbate interactions can fundamentally reshape phonon-assisted relaxation dynamics upon interband excitation. Our findings show that a surface adsorbate on a plasmonic metal can suppress both charge carrier cooling and vibrational energy relaxation, thus affecting both CT and photothermal pathways in Au-adsorbate systems. Our study of this model, well-defined sys-

tem, circumventing complicating solvent interactions, serves as a stepping stone for continued systematic exploration of other model plasmonic metal-adsorbate systems. Looking ahead, the application of advanced site-specific spectroscopic probes further promises to yield detailed insights into CT and ET processes in this class of systems.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

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