Direct observation of plasmonic hot-carrier energy distributions via single molecule transport measurements

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**Abstract:** Hot-carriers in plasmonic nanostructures, generated via plasmon decay, play key roles in applications like photocatalysis and in photodetectors that circumvent band-gap limitations. However, direct experimental quantification of steady-state energy distributions of hot-carriers in nanostructures has so far been lacking. We present transport measurements from single molecule junctions, created by trapping suitably chosen single molecules between an ultra-thin gold film supporting surface plasmon polaritons and a scanning probe tip, that can provide quantification of plasmonic hot-carrier distributions. Our results show that Landau damping is the dominant physical mechanism of hot-carrier generation in nanoscale systems with strong confinement. The technique developed in this work will enable quantification of plasmonic hot-carrier distributions in nanophotonic and plasmonic devices.

**One Sentence Summary:** Single molecule transport measurements are used to quantify the hot-carrier distributions in plasmonic nanostructures.

Hot-carriers, energetic electrons and holes with energy distributions that deviate significantly from equilibrium Fermi-Dirac distributions (*1*), are expected to arise in metallic nanostructures due to the non-radiative decay of surface plasmons. Such hot-carriers hold promise for the development of a variety of technologies, including plasmon-driven photochemistry (*2*–*5*), alternative solar-energy harvesting devices (*6*), and efficient photodetectors operating below bandgap (*7*–*9*). Central to the design and development of these applications is knowledge of the hot-carrier energy distributions (HCEDs) that are generated under steady-state conditions (*10*). While past work has tried to quantify HCEDs (*11*–*15*) a majority of this work has relied on first-principle calculations or semi-classical approaches, which involve assumptions on the dominant relaxation pathways of hot-carriers as well as material properties (*15*) that lead to significant uncertainties in the estimated HCEDs (*12*, *13*). In fact, recent calculations (*16*) have even suggested that the deviations from the equilibrium Fermi-Dirac distribution are negligibly small, questioning past calculations. Therefore, direct experimental observations are critical for obtaining detailed insights into the HCEDs and for rationally engineering the aforementioned technologies.

Here, we show how scanning probe-based techniques (*17*–*19*) that measure charge transport in single molecules, when combined with nanoplasmonic experimental methods, can be leveraged to directly quantify the steady-state HCEDs () in a key model system—a thin gold film that supports propagating surface plasmon polaritons (SPPs). Our basic strategy is to first create single molecule junctions (SMJs)—using carefully chosen molecules with appropriate transmission characteristics—between a plasmonic gold (Au) film and the Au tip of a scanning tunneling microscope (STM), and elucidate the current-voltage characteristics with and without plasmonic excitation at various voltage biases () (see Fig. 1A). The difference in the measured currents for the cases with () and without () plasmonic excitation, which we call the hot-carrier current , enables us to directly quantify .

To elaborate, as depicted in Fig. 1B & 1C, arises due to the generation of the non-equilibrium carriers under plasmonic excitation with an energy distribution . We note that the energy distribution represents the difference between and the equilibrium Fermi-Dirac distribution as . As explained in detail in the Supplementary Materials (*20*), and are related by:

|  |  |  |
| --- | --- | --- |
|  | , | (1) |

where is the transmission function of the SMJ, *e* is the elemental charge and *h* is the Planck constant. When SMJs that feature a sharp peak in are employed, is predominantly determined by the hot-carriers with energies close to the transmission peak, simplifying the above integral to ((*20*), section 1):

|  |  |  |
| --- | --- | --- |
|  | , | (2) |

where is the energy of the peak in with respect to the Fermi energy (*E*F). Eq. 2 relates to via a voltage and energy-independent constant scaling factor (). Therefore, by varying in the window , the steady-state HCEDs can be mapped within the energy window (Fig. 1C.

We used the molecules shown in Fig. 1D (labeled ***L1***, ***H1***, ***L2***) for experimental quantification of the HCEDs. Molecule ***L1*** represents a charge-transfer complex of quaterthiophene (T4) and tetracyanoethylene (TCNE) with terminal thiophenes containing gold-binding methyl sulfides, while the ***H1*** molecules, 3,4-ethylenedioxythiophene (EDOT), are flanked by two thiophenes with terminal thiophenes containing gold-binding methyl sulfides. The transmission characteristics of Au-***L1***-Au and Au-***H1***-Au SMJs are expected to be sharply peaked and dominated by the lowest unoccupied molecular orbital (LUMO) (*21*, *22*) and highest occupied molecular orbital (HOMO) (*23*), respectively. Finally, we also utilize ***L2***, 1,4-benzenediisonitrile molecules (see section 3 of (*20*) for additional details), SMJs created which are expected to feature weakly energy-dependent also dominated by the LUMO level (*24*).

Plasmonic gold films (thickness 6 nm and 13 nm), with integrated grating couplers, were fabricated on fused silica substrates (Fig. 1A) to excite SPPs and generate hot-carriers ((*20*), section 4). The 6 nm-thick gold film with grating coupler was first exposed to a solution containing ***L1*** molecules to create a monolayer of the molecules ((*20*), section 5). Next, we positioned a Au STM tip at a separation of ~1 (along the *x* direction) from the grating edge (Fig. S2). Subsequently, the Au film was covered with an immersion oil matching the refractive index of fused silica to create a symmetric optical medium around the film, and a was applied to the STM tip while grounding the Au film. We then employed STM break-junction technique (*17*, *18*) (see (*20*), section 2 for a detailed protocol) to identify the current through a Au-***L1***-Au SMJ. The peak in the current histogram created from over 2000 current vs displacement traces represents the most probable current ()—corresponding to a conductance of for a Au-***L1***-Au junction (Fig. 2A) under the absence of plasmonic excitation (*G*0 is the quantum of electrical conductance), in good agreement with prior work (*22*). Subsequently, we illuminated the gratings with a focused an 830 nm, linearly polarized laser beam ( power density) perpendicular to the grating strips, launching SPPs in the Au film (Fig. 1A). Concurrently, we measured the electrical current under laser illumination and found that the most probable current is larger than (Fig. 2A). We then determined the hot-carrier current as . The measured displayed a strong dependence on the laser polarization (Fig. 2C), consistent with the polarization dependent SPP excitation efficiency, indicating that the measured is due to the excitation of SPPs. Additional control experiments further confirmed that the measured is indeed due to hot-carrier effects and not due to an increased temperature or simple light-assisted transport ((*20*), section 6).

Next, we performed additional measurements from Au-***L1***-Au SMJs at the same location, while systematically varying from . The measured bias-dependent (Fig. S16A) displayed an asymmetric shape with a peak around 0.15V. Further, the transmission characteristics of Au-***L1***-Au junctions, necessary for determining the spectral distribution of hot carriers (see Eq. 1 and 2), were obtained using an experimental approach developed in (*23*) ((*20*), section 7). Figure 2D shows the obtained for Au-***L1***-Au junctions. Consistent with past work (*23*), we fit the measured with a Lorentzian and obtained the energy of the peak to be relative to with a peak width of 2.6 meV (red curve in Fig. 2D), confirming the sharp nature of the peak ((*20*), section 7) in good agreement with past computational work (*20*). Subsequently, we determined from the measured and of ***L1*** using Eqn. 2. The measured (see Fig. 3A) revealed the relative hot-electron energy distribution (HEED), displaying a peak around 100 meV followed by a decaying tail extending up to about 330 meV above . It should be noted that, as the transmission function peak enters the window between the quasi Fermi levels of the two contacts, extremely large currents flow through the molecular junction making the junction unstable and limiting the sweep window to and the energy window to with respect to ((*20*), section 7). However, this is not a fundamental limitation as additional measurements and analysis with Au-***L2***-Au SMJs enabled measurements of the HEED at higher energies, which revealed that there are negligibly few hot-electrons with energies beyond 0.4 eV (dashed line in the inset of Fig. 3A, (*20*), section 10).

To determine the hot-hole energy distribution (HHED), i.e. energies below , we repeated measurements of in Au-***H1***-Au SMJs for in the range of (Fig. S16B). Unlike for ***L1***, where large was observed for positive , no perceptible was recorded in ***H1*** junctions for positive . Instead, in ***H1*** junctionsincreased above the noise floor for below and peaked around . Next, we measured the transmission characteristics of Au-***H1***-Au junctions, and obtained the Lorentzian-shaped transmission characteristics shown in Fig. 2E, which features a peak at and a peak width of 6.8 meV, in good agreement with prior work (*23*). From the measured and , we obtained using Eqn. 2 over the energy range (Fig. 3B). The HHED featured a peak around and a decaying tail that extends to energies about with respect to .

To gain insights into the microscopic origin of our observations, we performed first-principle density functional theory (DFT) calculations (*11*) to compute the hot-carrier generation rates and subsequently employed the Boltzmann transport equation under the relaxation time approximation (*25*) to obtain the steady-state HCEDs ((*20*), section 11). For our calculations, we considered a geometry consisting of a Au film surrounded by a symmetric dielectric environment with a refractive index , mimicking the geometry in our experiments, which is known to support two plasmonic modes: a symmetric mode and an anti-symmetric mode with distinct dispersion relations (*26*–*28*).

The computed HCED arising from the symmetric plasmonic mode on a 6 nm-thick Au film, obtained using both an energy-dependent electron-electron collision rate from Landau’s Fermi liquid theory (FLT) (*29*) and an energy-independent scattering rate are shown in Fig. 4A. Additionally, electron-phonon scattering is included via an energy-independent relaxation rate (*30*). Note that these computational results are multiplied by a scaling factor so that the peak value is 1. The results obtained following FLT predict that hot-carriers are largely populated within the energy window of relative to *E*F—in excellent agreement with our experiments. In contrast, an energy-independent scattering rate results in hot-carriers in a larger range of energies (Fig. 4A, blue curve) that disagree with our experimental observations. These findings establish the validity of employing the energy-dependent electron-electron collision for modelling hot-carriers in plasmonic nanostructures.

To understand the effect of film thickness we measured the HCED in thicker (13 nm-thick) Au films. The measured HCED (Fig. 3C & 3D) showed that the hot-carriers are mostly populated around *E*F. Besides, the total number of hot-carriers (sum of hot-electrons and hot-holes, ) was found to be ~40% smaller than those measured on 6 nm film. The observed reduction in the magnitude of HCED in thicker films can be attributed to the effect of surface-assisted absorption—Landau damping (*13*, *15*, *25*) (see relevant discussion in (*20*), section 11). To quantify the role of Landau damping, we computed the HCED in a 13 nm film arising from the symmetric plasmonic mode, and scattering rates from FLT (Fig. 4A, red curve). As evident from Fig. 4A, the generated hot-carriers are populated close to *E*F, similar to the 6 nm film. However, about 43% fewer hot-carriers are generated in the 13 nm film, in good agreement with our experiments.

To elucidate the distance-dependence of the observed hot-carrier generation rates, we measured for Au-***L1***-Au SMJs at a for varying separations (*d*) from the grating edge on a 6 nm-thick gold film (Fig. 4C). The measured decreases as the separation from the edge of the gratings increases and drops close to zero for . To understand the observed distance dependence, we simulated (using the Lumerical FDTD package) the intensity profile in the 6 nm film upon illuminating the grating coupler with an 830 nm laser. A beating profile was observed close to the gratings (Fig. 4D), which we attribute to the interference between the two plasmonic modes ((*20*), section 12 and inset in Fig. 4D). However, for the symmetric mode decays while the anti-symmetric mode shows very little decay. Since there are no observed hot-carriers at large separations, despite the presence of the anti-symmetric mode, we conclude that the contribution of the anti-symmetric mode to hot-electron generation is negligible. Additional calculations (Fig. 4B) confirmed that the anti-symmetric mode is indeed much less effective in generating hot-electrons, resulting in 400-times (30-times) fewer carriers, in comparison to the symmetric mode for the 6 nm (13 nm)-thick film.

Our scanning probe-based approach combines single molecule quantum transport measurements and nanoplasmonics to directly map the steady-state energy distributions of hot-carriers. The approaches developed will enable fundamental insights into hot-carrier generation processes and are critical for future hot-carrier assisted technologies.

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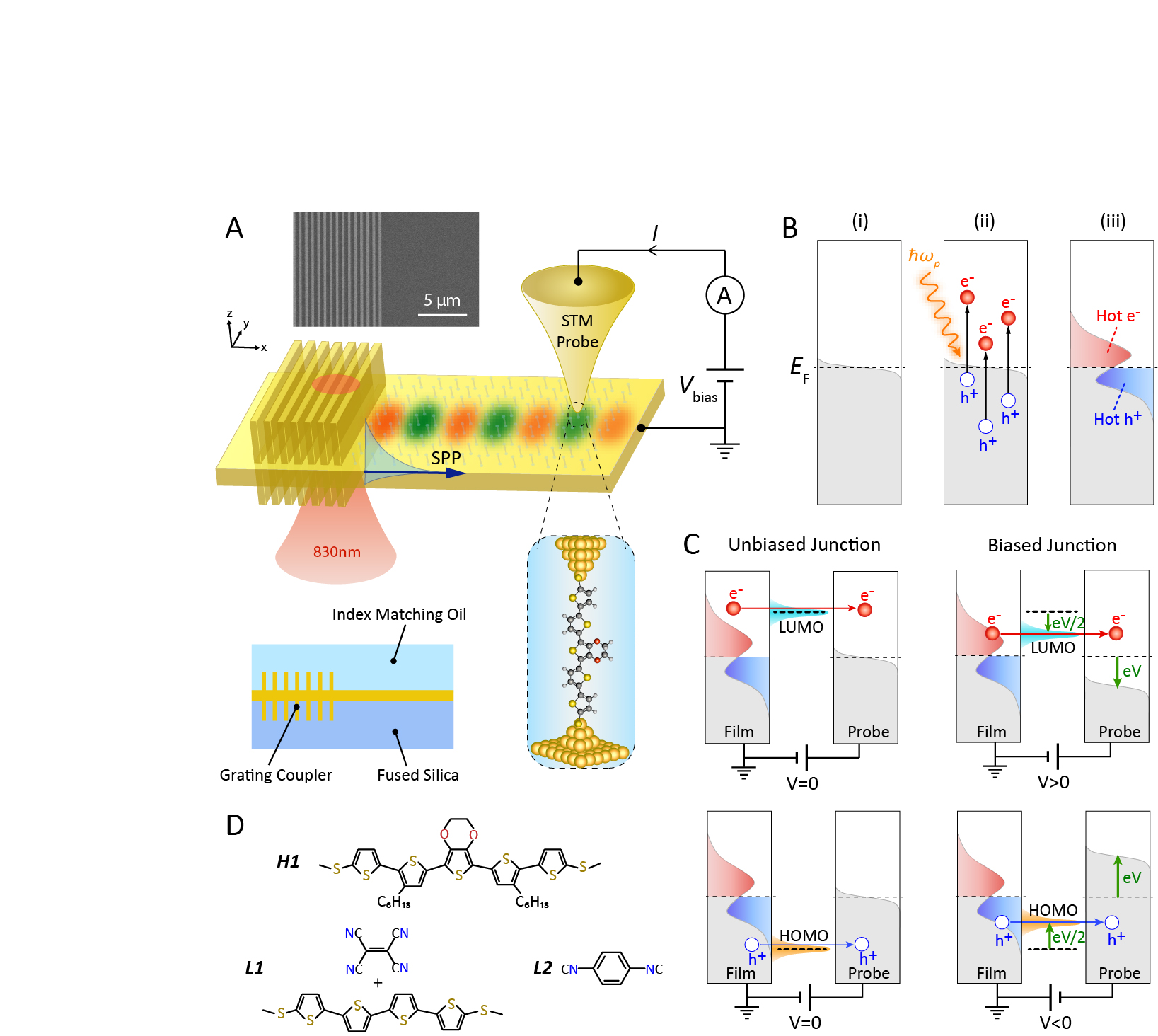
Supplementary Materials:

Materials and Methods

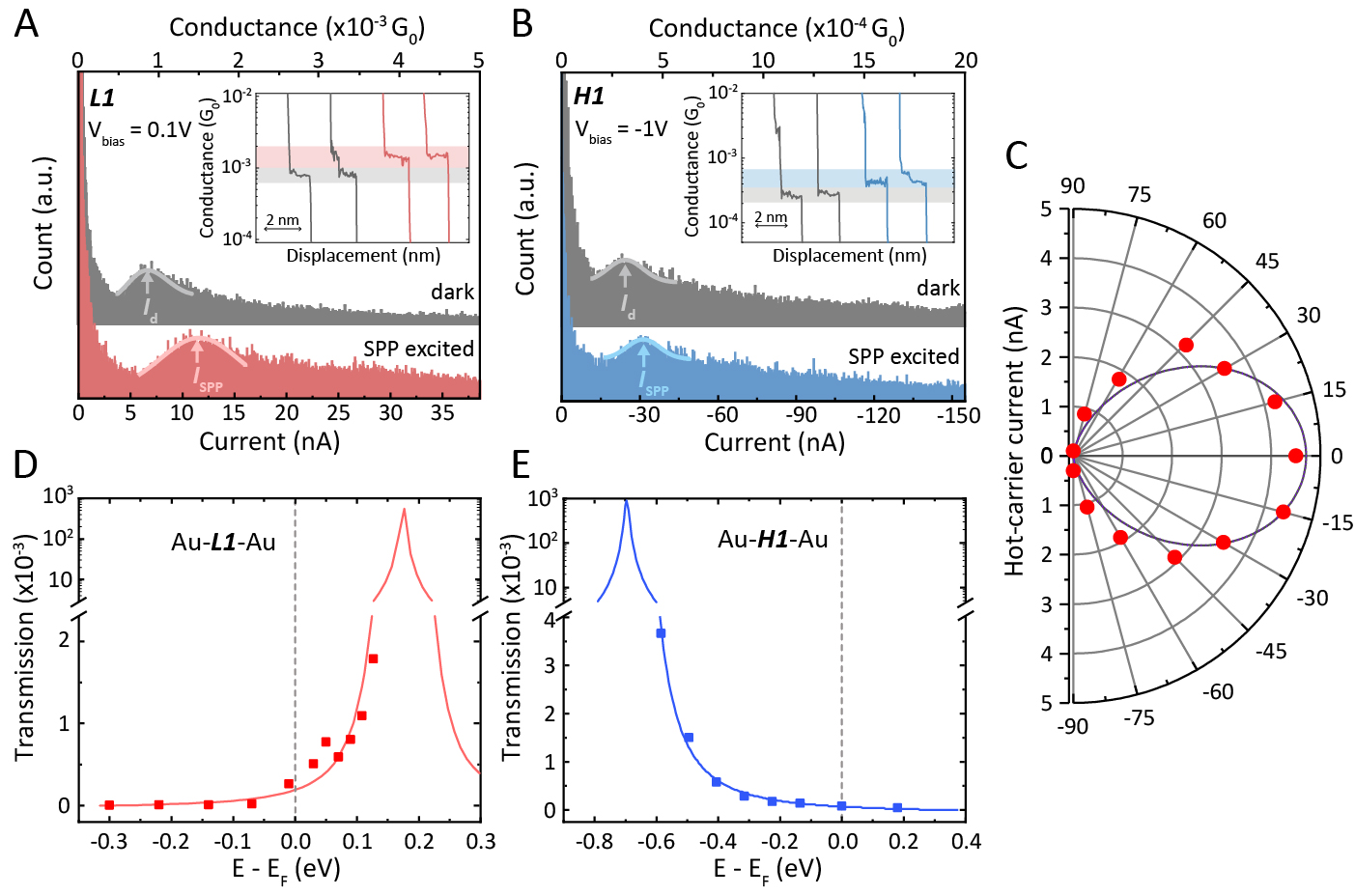
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Figures S1 – S23

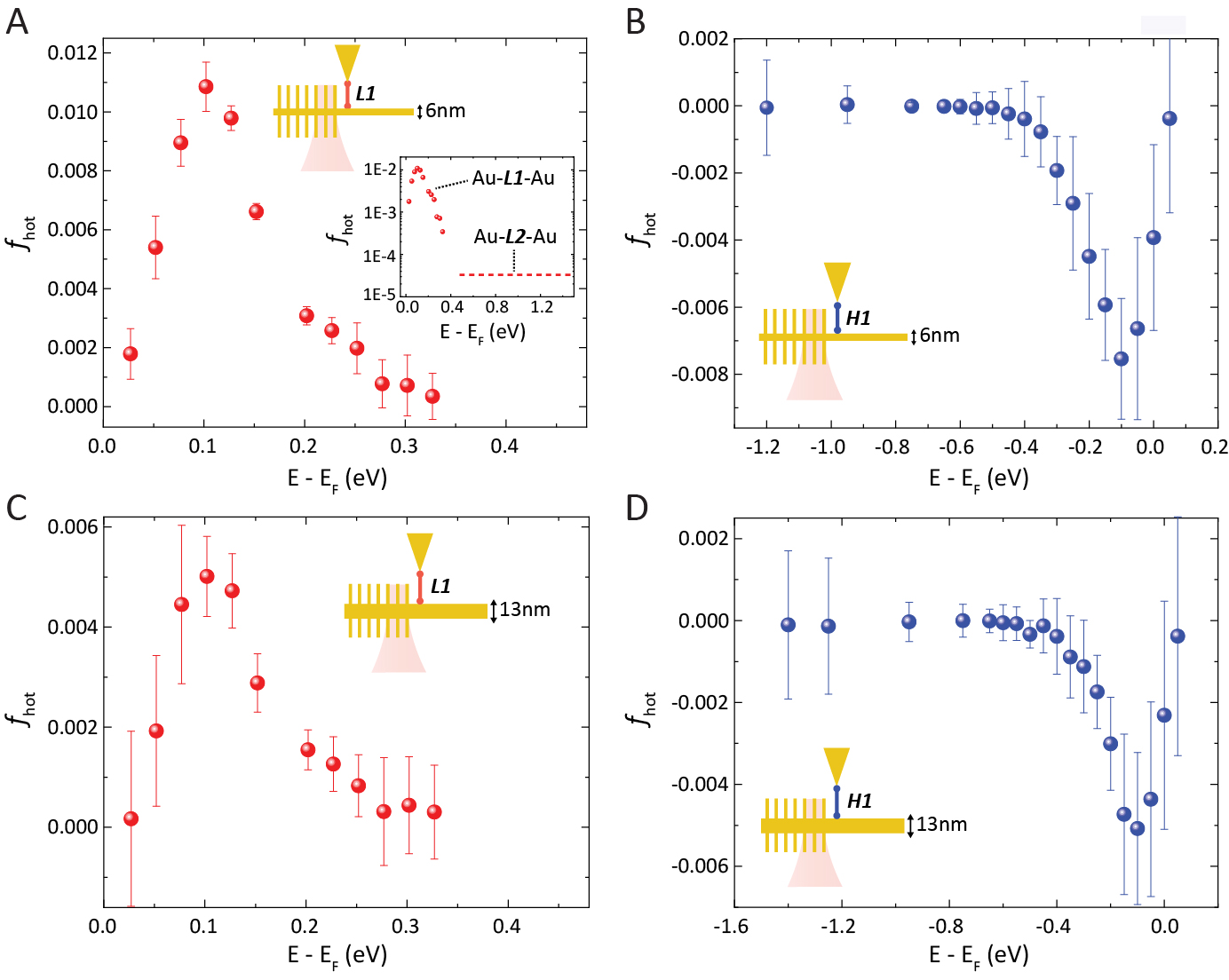
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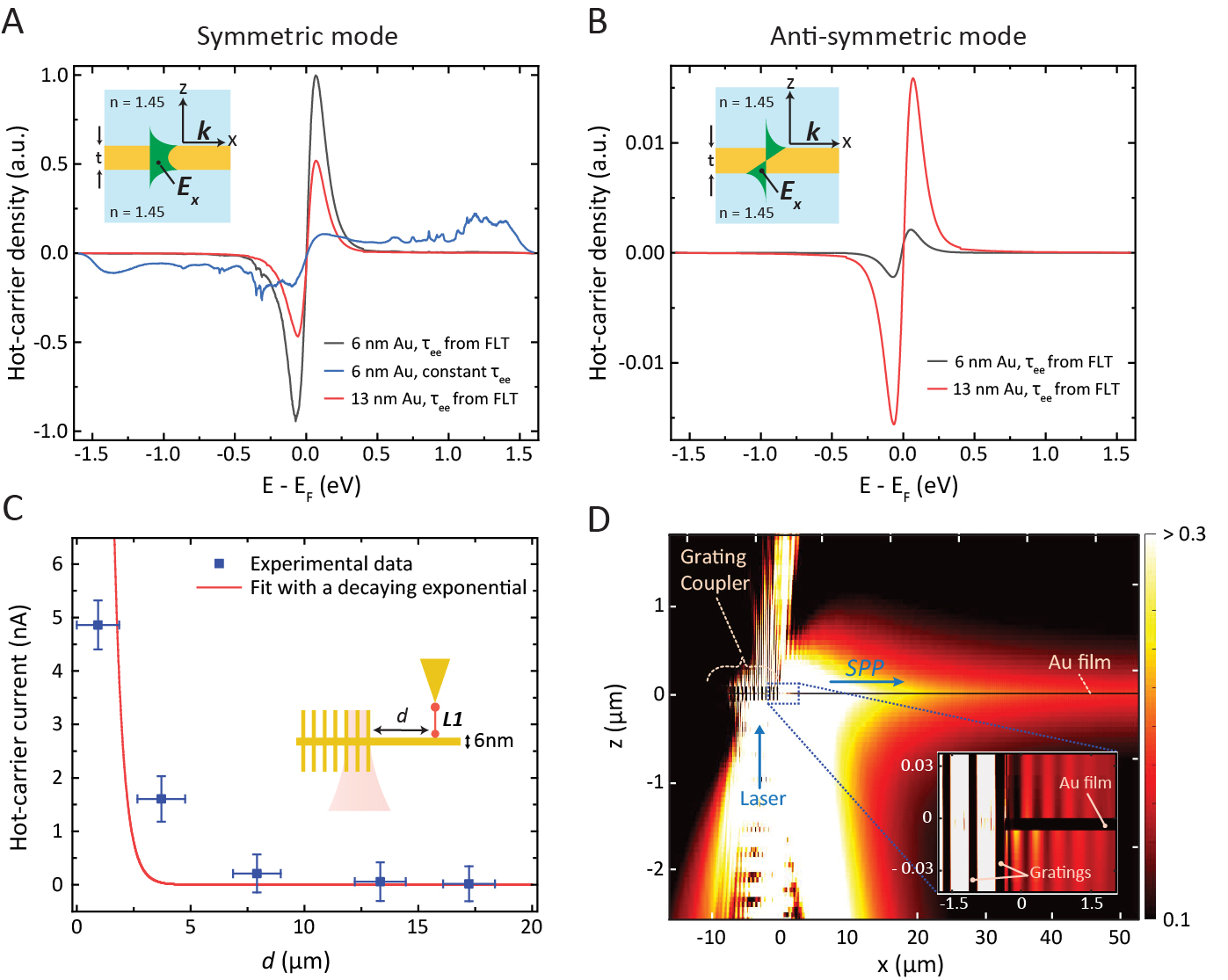
**Fig. 1: Experimental setup and strategy to map hot-carrier energy distributions (HCEDs). ­­**(**A**) Schematic of the experimental set-up. Single molecule junctions (SMJs) are formed between a grounded nanodevice (Au film with integrated grating coupler) and a biased Au STM probe. Surface plasmon polaritons (SPPs) are excited by illuminating the grating coupler with 830 nm CW laser. The SEM image shows a fabricated nanodevice on 6 nm Au film. The bottom left graphic represents a cross-section of the nanodevice covered with index matching oil. (**B**) Schematic of hot-carrier generation. (i) Equilibrium Fermi function. (ii) Non-radiative decay of SPP energy () generates electron-hole pairs, resulting in (iii) non-equilibrium distribution of hot-electrons and holes. (**C**) Schematic showing how LUMO or HOMO-dominated SMJs with sharp transmission peaks selectively transmit hot-carriers. Biasing the junctions shifts the transmission peak with respect to the equilibrium Fermi level enabling quantification of HCED. (**D**) Structures of molecules used in this work.



**Fig. 2: Hot-carrier induced changes in SMJ currents, polarization-dependence, and transmission characteristics of *L1* and *H1* molecules.** (**A**) Current and conductance histograms of Au-***L1***-Au SMJs from over 2000 traces of dark (grey) and SPP-excited (magenta) measurements at a voltage bias of 0.1V. Gaussian fits to the histogram peaks are represented as solid lines and the vertical arrows indicate the most probable conductance and current. Inset shows representative conductance traces following the same color coding. (**B**) Same as (**A**), but for Au-***H1***-Au junctions and -1.0V bias voltage. The grey and blue colors correspond to measurements from dark and SPP-excited cases, respectively. (**C**) Polarization-dependence of the hot-carrier current () for Au-***L1***-Au junctions (red circles) at 0.1V bias voltage along with the best-fit dependence (black line). (**D**) and (**E**) Measured transmission functions (note the linear and logarithmic scales) of Au-***L1***-Au and Au-***H1***-Au junctions along with the Lorentzian fits (solid lines).



**Fig. 3: Energy distributions of hot-carriers in 6 nm and 13 nm-thick Au films.** (**A**) The measured HEED in a 6 nm Au film obtained from measurements on Au-***L1***-Au and Au-***L2***-Au SMJs. The energy distribution in the range up to 0.33 eV was measured with Au**-*L1***-Au junctions. The inset shows the HEED on a log scale and the dashed line represents the upper bound on the average in the energy window as determined with Au-***L2***-Au junctions. (**B**) The measured HHED in a 6 nm Au film using Au-***H1***-Au junctions under otherwise identical conditions compared to (**A**). (**C**) & (**D**) Measured HCEDs for 13nm Au film but otherwise as for (**A**) & (**B**). The error bars correspond to the propagated errors from uncertainties in the measured .



**Fig. 4: Computed HCEDs, distance dependence and intensity profile.** (**A**)­ ­Computed HCEDs in 6 nm- and 13 nm-thick Au films, arising from the symmetric plasmonic mode with electron-electron scattering rates from either Fermi liquid theory (FLT) or an energy-independent scattering rate. Inset shows the employed geometry and mode profile. (**B**) Same as (**A**), but for the anti-symmetric plasmonic mode. Note that the y-axis scale is smaller in (**B**) compared to (**A**). (**C**) Measured through Au-***L1***-Au SMJs (at 0.1V bias voltage) for varying separations *d* between the probe tip and the grating edge. Error bars represent uncertainties in *d* and . The red curve is an exponential fit constrained to have a decay length of 405 nm, corresponding to the symmetric mode’s decay constant in 6 nm gold film (see (*20*), section 14).(**D**) Simulated intensity profile normalized to the incident field intensity upon illuminating the gratings with a focused 830 nm laser (spot size of 5.6 m). Inset shows the intensity profile near the grating edge. The color map of the inset is adjusted to show the beating pattern, and is different from the main panel color map.