Hot-carrier transfer across a nanoparticle-molecule junction: The importance of orbital hybridization and level alignment

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While direct hot-carrier transfer can increase photo-catalytic activity, it is difficult to discern experimentally and competes with several other mechanisms. To shed light on these aspects, here, we model from first principles hot-carrier generation across the interface between plasmonic nanoparticles and a CO molecule. The hot-electron transfer probability depends non-monotonically on the nanoparticle-molecule distance and can be effective at long distances, well outside the region of chemisorption; hot-hole transfer on the other hand is limited to shorter distances. These observations can be explained by the energetic alignment between molecular and nanoparticle states as well as the excitation frequency. The hybridization of the molecular orbitals is the key predictor for hot-carrier transfer in these systems, emphasizing the need to include the effects of ground state hybridization for accurate predictions. Finally, we show a non-trivial dependence of the hot-carrier distribution on the excitation energy, which could be exploited when optimizing photo-catalytic systems.

I. INTRODUCTION

Plasmonic metal nanoparticles (NPs) are fundamental components in several emerging technologies, including sensing,1,2 light-harvesting,3 solar-to-chemical energy conversion4–6 and catalysis.7–10 The properties that set these materials apart for these applications are their high surface-to-volume ratios and high optical absorption cross sections at visible frequencies,11,12 the latter being due to the presence of a localized surface plasmon (LSP) resonance.13 In particular plasmonically-driven catalysis is an active research field, addressing important chemical reactions such as ethylene epoxidation, CO oxidation or NH3 oxidation that are catalyzed by illuminating NPs, e.g., of the noble metals Ag,10,14 Au5,6,15 or Cu5,9

The LSP, which is a collective electronic excitation, is excited by absorption of light and decays within tens of femtoseconds4,16–22 into a highly non-thermal (usually referred to as “hot”) distribution of electrons and holes.23–29 Chemical reactions can then be catalyzed by hot carriers (HCs) transiently populating orbitals of nearby molecules,4,30 which can, e.g., lower reaction barriers.18 Two variants of this process can be distinguished. In the direct HC transfer process31 (also known as chemical interface damping) the LSP decays into an electron-hole pair, where one of the carriers is localized on the reactant molecule and the other on the NP. In the indirect HC transfer process both carriers are generated in the NP, and at a later time scattered into molecular orbitals. The efficiency and importance of these processes as well as their competition with thermal effects, is still a matter of intense debate,18,32–35 highlighting the importance of more detailed atomistic studies. The direct HC transfer process is promising in terms of efficiency and selectivity,14,30 and has been studied experimentally,36 in theory,31 and by computational ab-initio models.20,21,37 Typically the focus lies on understanding HC generation at surfaces,36,38 but there has not yet been a detailed account of the dependence of HC transfer on molecular position and orientation, and whether there are handles for tuning HC devices to particular molecules in all probable states of thermal motion. Yet these aspects are crucial for direct HC transfer processes, which exhibit an intricate dependence on the hybridization of molecular and surface states as also shown in this work.

In this work, we study plasmon decay and carrier generation across a NP-molecule junction, which is the initial step in the direct HC transfer process. We consider plasmonic Ag, Au, and Cu NPs in combination with a CO molecule, whose excitations are energetically much higher than the plasmon resonance of any of the NPs considered here. In a real-time time-dependent density functional theory (RT-TDDFT)39 framework, we drive the system with an ultra-fast laser pulse to induce a plasmon. We simulate the electron dynamics in the system until the plasmon has decayed, and then analyze the distribution of carriers over the ground state Kohn-Sham (KS) states. To this end, we employ and extend the analysis methods previously developed by us.19–21

We consider a wide range of geometrical configurations. Specifically, we treat (111) on-top, (111) face-centered cubic (fcc), (100) hollow and corner sites of molecular adsorption on the NP and various distances between the molecule and NP. We map out the HC transfer efficiency as a function of the NP-molecule geometry (adsorption site, distance, molecular bond length), excitation energy, and material (Ag, Au, Cu).

The article is structured as follows. We present and discuss our results for Ag NP+CO systems driven by a laser pulse tuned to the LSP resonance in Sect. II A, Sect. II B and Sect. II C. In Sect. II D we quantify the dependence of carrier generation on the pulse frequency, including Ag, Au, and Cu NPs. Finally, in Sect. III we discuss the implications of our findings. Details concern-

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ing our methodology, the systems under study as well as the parameters used in computations are provided in Sect. A.

II. RESULTS AND DISCUSSION

A. Adsorption geometry-dependent carrier generation in Ag

We consider the CO molecule at a range of distances from the Ag$_{201}$ NP (111) on-top, (111) fcc, (100) hollow and corner sites. The plasmon (3.8 eV, Fig. 1a) and first optical excitation of CO (14.5 eV, Fig. S1) are not resonant and the optical response of the combined NP+CO system is not strongly dependent on geometry (Fig. S2).

The bond length of CO, which is 1.144 Å in the free molecule, increases when adsorbed to the NP (corner: 1.150 Å, (111) on-top: 1.151 Å, (111) fcc: 1.170 Å and (100) hollow 1.184 Å). Higher coordination numbers for the C atom thus result in larger bond lengths. This is in agreement with previous studies on the extended (111) Ag surface, and can be understood by considering that as C shares more electron density in bonds with metal atoms, the CO bond is weakened.

As we vary the NP-CO distance (Fig. 1b), we observe minima in the binding energy curves around 250 meV-500 meV at 1.5 Å-2.3 Å (Fig. 1c). Here, we define the binding energy as

$$E_{\text{bind}}(d) = E^{\text{site}}(d) - E^{\text{NP}} - E^{\text{mol}} \tag{1}$$

where $E^{\text{NP}}$ and $E^{\text{mol}}$ are the energies of the NP and molecule, respectively, taken from two separate calculations, representing infinite separation. Note that in this definition (Eq. 1), we take $E^{\text{NP}}$ and $E^{\text{mol}}$ as the energies of the NP and molecule as in the relaxed configuration for the specific site, emphasized by the superscript (site). Allowing the molecule to relax at each distance effectively widens the adsorption curve but does not affect the main conclusions drawn here (Fig. S3, Fig. S4). However, the bond length reduces, however, the degrees of freedom and simplifies the following discussion, whence we adopt this constraint.

We drive the Ag NP+CO system with a Gaussian laser pulse tuned to the LSP frequency $\hbar \omega = 3.8$ eV. Within the first tens of femtoseconds a plasmon forms in the NP and decays into resonant excitations, for which the electron-hole energy difference equals $\hbar \omega$. The plasmon formation and decay process in similar systems has previously been studied in detail by our group and is not covered here.

We then measure the fraction of generated electrons in the molecule (Eq. A19) after plasmon decay (Fig. 1c). While intuition would suggest this quantity to decrease monotonically with decreasing wave function overlap at increasing distances, we find the fraction of generated HCs to be of similar magnitude measuring between 0.5 and 2% over a wide range of distances with several site specific features. A smooth decay to zero only occurs beyond 4 to 5 Å. Below this threshold several of the sites feature one or two peaks, including near 2.1 Å and 3.3 Å for the (111) on-top site, 2.7 Å for the (100) hollow site and 2.7 Å and 3.9 Å for the corner site. Only the (111) fcc site appears relatively feature-less.

By contrast, the binding energies depend smoothly on distance and approach zero already at 3 to 4 Å. The landscape of electron generation on the molecule thus extends further than the features in the potential energy surface and is more sensitive to the underlying shifts in eigenenergies and wave function overlaps. Our findings imply that across-interface HC generation can be effective even at quite long distances (up to 5 Å) from the NP, and does not require molecular adsorption.

The fraction of holes generated on the molecule (Eq. A18), on the other hand, decays smoothly with distance (Fig. 1d) reaching a maximum of 0.2% to 0.8%.

B. Origin of the HC generation distance dependence

To explain the rich behavior of the across-interface electron generation as a function of distance we study the molecular PDOS (Fig. 2a,c) and the energy distribution of HCs generated on the molecule (Eq. A21, Fig. 2b,d). We note that as the molecule only contains a small fraction of the electrons in the system, the NP PDOS makes up the most part of the total density of states (DOS) and is practically independent of distance. The molecular PDOS, however, is strongly site and distance-dependent. At long distances the PDOS is comprised of a single LUMO level at 2.8 eV, which shifts to lower energies with decreasing distance, eventually splitting into several branches. Most of these branches are above the Fermi level (Fig. S5) and thus represent unoccupied hybridized states.

The hot electron distribution in the molecule clearly mirrors the shape of the PDOS as electrons are generated in unoccupied molecular levels. The distribution of electrons in each PDOS branch is, however, not simply proportional to the corresponding PDOS weight. As the transitions ($\varepsilon_i \rightarrow \varepsilon_a$) induced by the pulse are resonant with the pulse frequency ($\varepsilon_a - \varepsilon_i = \hbar \omega_{\text{pulse}} = 3.8 \pm 0.37$ eV, the value after ± denotes the half-width at half-maximum of the Gaussian pulse in frequency space), the electron distribution is determined by the energetic alignment of the molecular PDOS with the NP PDOS. It is worth noting that various states in the NP couple with differing strength to the molecular states; the alignment with particular peaks in the NP PDOS is therefore important (Fig. S6). The across-interface electron generation is thus enhanced at energies $\varepsilon$ where (1) the molecular PDOS is large at $\varepsilon$, (2) the NP DOS is large at $\varepsilon - \hbar \omega$ and (3) the transition dipole moment between the corresponding NP and molecular states is sizable. It is im-
FIG. 1. Geometry dependence of HC generation in $\text{Ag}_{201}$ NP + CO. (a) Optical spectrum of the bare NP. The frequency $3.8\text{eV}$ of the driving laser is marked by an arrow above the spectrum. (b) Model of the NP with the axes along which the NP-molecule distance is varied. (c-d) Fractions of generated electrons (c) and holes (d) on the molecule (Eq. A19) after 30 fs and binding energies (Eq. 1) as a function of distance and site.

FIG. 2. Level alignment between molecular and NP PDOS for (111) on-top (a-c) and corner (d-f) sites. (a, d) Molecular PDOS as a function of distance. As the molecule approaches the NP the LUMO shifts to lower energies, eventu- ally splitting into several branches. The PDOS for the NP and molecule at far separation are indicated above the plot, where the NP PDOS has been shifted by the pulse frequency. Shaded regions correspond to (a selection of) large values in the shifted NP PDOS. (b, e) Electron distribution as a function of distance. (c, f) The fraction of electrons generated in the molecule.

important to emphasize that it is the combination of these effects that dictates the response. It is, however, usually much simpler to obtain the PDOSs than the transition dipole matrix elements, and we may assess the basic possibility for HC transfer already on this basis. This is apparent, e.g., in the decomposition of the electrons distribution in terms of the underlying single-particle excitations (Fig. S6). The variation of the HC transfer probability with distance is the result of transitions from two occupied states $0.95$ and $1.20\text{eV}$ below the Fermi energy and one unoccupied state $2.46\text{eV}$. The transitions involving these three states at $3.41$ and $3.66\text{eV}$ are slightly different from the excitation frequency of $3.8\text{eV}$ considered in this section but are still activated due to the finite linewidth of the excitation pulse. In fact, in Sect. IID below, we will find that a slight reduction in the excitation frequency leads to a notable increase in the HC transfer probability.

In a similar manner we can understand the across-interface generation of holes, with the rule that an occupied state $\varepsilon$ in the molecule must align with a peak in the NP PDOS at $\varepsilon + \hbar\omega$. As the CO highest occupied molecular orbital (HOMO) level is at $-4.8\text{eV}$ in the free molecule (long distance limit), hole generation is not possible with the pulse frequency $3.8\text{eV}$. Transfer is only possible at close distances where hybridized branches of the HOMO and LUMO appear in the region $-3.8\text{eV} < \varepsilon < 0\text{eV}$, beginning at distances around $2.5\text{Å}$. (Fig. S5).

The energetic level alignment is thus a good descriptor in predicting across-interface HC generation. Other factors, such as the amount of wave function overlap and the orbital momentum character of states, play a role, i.e., in determining the coupling strength between occupied and unoccupied states, but the energetic level alignment is sufficient to qualitatively explain the distance and site dependence. In the case of $\text{Ag}_{201}$ with $3.8\text{eV}$ pulse frequency the constructive contributions to the LSP stem from delocalized sp-band states that also have a larger spatial extent. This provides a rationale for the rather long-ranged effect that we observe here. Based on this
Electron distribution (1/eV)

\[ \times 10^{-8} \]

![Graph showing electron distribution](image)

| Energy (eV) | Molecule | Corner site atom |
|------------|----------|-----------------|
| 0.0        | 0.6 A    | -               |
| 0.5        | 3.9 A    | -               |
| 1.0        | 3.5 A    | -               |
| 1.5        | 3.1 A    | -               |
| 2.0        | 3.0 A    | -               |
| 2.5        | 2.8 A    | -               |
| 3.0        | 2.6 A    | -               |
| 3.5        | 2.3 A    | -               |
| 4.0        | 1.9 A    | -               |

FIG. 3. Energy distribution of electrons generated on the molecule and on the NP corner site that the molecule approaches. While the former varies non-monotonically, the latter is practically unchanged with distance.

To further emphasize that the energy distribution of electrons generated on the molecule depends on energetic level alignment, we compute the energy distribution of electrons on the nearest metal atom (the integral of Eq. A21 in the metal-atom Voronoi cell) as a function of distance (Fig. 3). We focus specifically on the corner site, where the distance dependence of the electron distribution on the molecule exhibits two clear maxima. We find that the electron distribution on the adsorption site is practically distance-independent.

Only at the smallest considered distances does the electron distribution on the molecule resemble the electron distribution at the adsorption site on the metal. Hence it is not enough to know the electron distribution on surfaces and surface sites for a bare NP to predict across-interface electron generation in combined NP + molecule systems. Equipped with distributions for the bare NP alone one misses for example that about 2 times more electrons are generated at 2.5 Å for the corner site, than at 1.9 Å. In other words, the surface electron distribution is an insufficient predictor for across-interface electron generation.

D. Adsorption geometry and pulse frequency-dependent HC generation

We now extend our study to also include Au and Cu. The s-electrons have nearly identical DOSs in the Ag_{201}, Au_{201} and Cu_{201} NPs but the d-band onsets differ (Ag: 3.7 eV, Au: 2.1 eV, Cu: 2.3 eV below the Fermi level; Fig. S7). As a consequence of the earlier d-band onset Au_{201} and Cu_{201} lack the well defined LSP peak of Ag_{201} (Fig. 4a). The binding energy curves are also similar to Ag, with the main difference that the molecule binds more strongly and closer to Cu (Fig. S8).

We drive the NP+CO with a Gaussian laser pulse (Ag: frequency 3.8 eV, Au: 2.5 eV, Cu: 2.7 eV) and measure the fraction of electrons generated on the molecule (Fig. 4b-e). We observe similar trends in Ag and Cu, both exhibiting peaks near 2.1 Å for the (111) on-top site, 2.7 Å for the (100) hollow site and 2.7 Å and 3.9 Å for the corner site. Only the 3.3 Å peak in the (111) on-top site of Ag lacks a counterpart in Cu. In contrast to Ag and Cu, the Au NP shows smooth trends, without pronounced peaks, of decreasing electron generation on the molecule with increasing distance.

The similarity in electron generation for Ag and Cu can be explained by a similar distance dependence of the molecular orbital hybridization (Fig. S5). We note that while the resonance condition is not the same for Ag and Cu (\( \omega = 3.8 \) eV and 2.7 eV, respectively), the similar energy-spacing between hybridized molecular levels is enough to yield similar electron generation curves. The 3.3 Å peak is the only clear feature that is missing in Cu, the reason being that the molecular orbital is too far from the Fermi level (2.8 eV, to be compared to \( \omega = 2.7 \) eV). The hybridization behavior in Au differs from the behavior in Ag and Cu. At long distances the CO LUMO is further from the Fermi level in Au than in Ag or Cu (due to Au having a higher work function, and us considering different bond length of the molecule for each metal), preventing electron generation. As the distance decreases the orbital hybridizes more strongly, splitting into more branches. As a consequence, at small distances there are more PDOS branches in which electron generation occurs, leading to a smoother distance dependence.

Based on our observations we should expect the pulse frequency \( \omega \) to act as a handle for tuning the electron generation through the approximate (barring electron-hole coupling) resonance condition \( \varepsilon_a - \varepsilon_i = \omega \). Indeed, the electron generation depends non-monotonically on both distance and pulse frequency (Fig. 5a-c). For example, by lowering the pulse frequency we can get rid of the dip in electron generation at 2.9 Å for the Ag (111) on-top site; using \( \omega = 3.1 \) eV the feature at the same distance instead becomes a maximum. Choosing the pulse frequency appropriately the fraction of electrons generated on the molecule can be as high as 8.9% for Ag (distance 2.7 Å, \( \omega = 3.1 \) eV), 1.1% for Au (distance 1.9 Å, \( \omega = 2.2 \) eV), and 2.3% for Cu (distance 2.1 Å,
FIG. 4. Geometry dependence of electron generation in Ag$_{201}$, Au$_{201}$ and Cu$_{201}$ NPs+CO. (a) Optical spectra of the bare NPs. (b-e) Fractions of generated electrons on the molecule (Eq. A19) after plasmon decay as a function of distance and site with pulse frequency 3.8 eV (Ag), 2.5 eV (Au) and 2.7 eV (Cu).

$\hbar \omega = 2.2$ eV). While the electron generation in the Ag and Cu systems shows a complex dependence on pulse frequency and distance, in the case of Au, it is almost monotonic in both dimensions. However, in both endpoints of the considered pulse frequencies the behavior for Au becomes more interesting; at low frequencies there is electron generation at long distances, due to the free-molecule LUMO falling into the relevant energy range.

In the case of Ag (Fig. 5d) and Cu (Fig. 5f), holes are generated at small distances (where hybridized branches of the LUMO orbital are below the Fermi energy; Fig. S5)
with a weak dependence on pulse frequency. For Au (Fig. 5e) hole generation becomes relatively strong at intermediate distances (3 - 5 Å) and large pulse frequencies. This behavior originates from the HOMO orbital, which in the long-distance limit resides 3.9 eV below the Fermi energy, but shifts to lower energies with decreasing distance (i.e., out of the range εₐ - ε₁ = ℏω, εₐ > 0, thus limiting hole generation).

The frequency of the exciting light is thus an excellent handle for tuning the fraction of carriers generated on the molecule, which is especially interesting in applications where selectivity is important. In molecules with several orbitals close enough to the Fermi energy to be optically accessible, the generation of electrons in one orbital could be favored over the other. It is, however, important at this stage to remember that changing the pulse frequency also changes the total optical absorption and thus the total number of generated carriers. We therefore also consider the total, pulse-frequency and distance-dependent, amount of electrons generated on the molecule (Fig. S9, that is, contrary to before, without expressing it as a fraction of electrons generated in the entire NP+CO system). In particular for the Ag NP, which has an exceptionally sharp absorption spectrum, the pulse dependence is affected, with a maximum in total electron generation on the molecule occurring using a pulse frequency of 3.6 eV (to be compared to a maximum in the fraction of electrons generated on the molecule at 3.1 eV). As a final note, we point out that it should be possible to simultaneously tune the pulse frequency to the desired resonance condition εₐ - ε₁ = ℏω, and the LSP resonance of the NP (thus the optical absorption) to the pulse frequency, by taking advantage of the fact that the LSP is more sensitive the size and shape of the NP than, e.g., the DOS.

### III. CONCLUSIONS AND OUTLOOK

In this study we have investigated the geometry dependence of HC generation across noble metal-molecule interfaces due to plasmon absorption and decay. We have found that typically up to 0.5 - 3% of all electrons generated in the system end up on the molecule after plasmon decay, even up to distances of 5 Å, which is well outside the region of chemisorption. By tuning the excitation frequency, we are able to achieve up to 8.9% electrons generated in the molecule, at the expense of lower absolute amount of electrons generated. These findings suggest that direct HC transfer is a relevant process in plasmon decay, and that the process does not require chemisorption of molecules to the absorbing medium.

We have also shown that the fraction of generated electrons on the molecule depends on the geometry of the molecule and NP in rather intricate fashion. This geometry dependence can be understood in terms of the energy landscape of hybridized molecular orbitals; as an orbital shifts so it is resonant with certain peaks in the NP PDOS an increase in the probability for HC transfer can be expected. The distance-dependent behavior of the hybridization differs enough for the various sites so that also the carrier generation differs. For larger NPs, these effects could be less important, as the DOS would be smoother.

In HC transfer processes the rate of charge carrier generation across the metal-molecule interface is in competition with various loss channels, such as the rates of reemission, and scattering and subsequent thermalization of excited carriers with phonons, surfaces, and other carriers. As these loss channels are currently beyond the reach of our calculations, we have to view our results as an upper bound on the efficiency of HC transfer, i.e., out of all photon absorption events that occur, up to 0.5 - 3% (or 8.9% when tuning the excitation frequency) result in electron transfer to the molecule. It is worthwhile to point out that HC generation is a quantized process, where it is very unlikely that there is at one time more than one excited plasmon at a time, under illumination conditions that are realistic for energy-harvesting applications. Each plasmon decays into one electron-hole pair where one carrier can be either in the molecule or in the metal, and we should thus consider our computed fractions as probabilities.

While the HC transfer landscape has a detailed structure, it is important to remember that in reality both the molecule and the NP are subjected to thermal motion. Since it is the weakest interaction in the combined system, one can expect the relative motion of NP and molecule to have the most pronounced thermal effect on level alignment, effectively broadening the peaks in the HC transfer probability curves. Considering $kT \approx 25 \text{ meV}$ at room temperature and the calculated binding energy curves (Fig. 1c), we should expect the molecule to move much less than 1 Å along the distance axis, but in reality the molecule is free to move laterally as well as rotate. Sampling the landscape of HC transfer in the full space of molecular movement is a high-dimensional problem that can be addressed in future work. For the purpose of a quantitative comparison to experimental realizations, it is crucial to consider that while metal states are accurately described with our level of theory, molecular states are not. We should thus expect transfer maxima to occur for different geometrical configurations, due to slightly shifted (hybridized) molecular orbitals; however, our general conclusions are still valid.

The importance of ground state hybridization for HC transfer implies that theoretical modeling should not be restricted to considering bare metal surfaces, without taking interactions with molecules into account. The distance-dependent hybridization of molecular orbitals should be explicitly taken into account for meaningful predictions. Our results suggest that since already the ground state of the hybridized system is a good descriptor for prediction of HC generation on molecules, rapid screening of candidates of good systems can be performed, without conducting expensive real-time simula-
tions.

We close by commenting on the possibilities for tuning HC transfer suggested by the results of this study. HC devices can be designed by tuning the resonance condition to achieve a desired purpose; handles for tuning to a certain molecular orbital are the NP DOS, surface substitutions that affect the hybridization of the orbital, and the frequency of the incoming light. As we have demonstrated, the tuning of the latter influences the absorption cross section so that there is a trade-off between high fraction of carriers transferred and high amount of carriers generated in total. It is possible, however, to shift the absorption maximum with a rather small impact on level alignment, by modifying the NP shape and size, so that there is a maximum in both absorption and transfer. In this way one ought to be able to maximize HC transfer. Furthermore, the sharp LSP resonances of Ag NPs could possibly be utilized in the design of highly selective catalysts that work with broadband (solar) light; if the NP PDOS consists of one particularly strong peak, and that peak is resonant to one specific molecular orbital with the frequency of the LSP resonance, then transfer to that specific orbital will be preferred over transfer to other orbitals.

DATA AVAILABILITY

The data generated in this study are openly available via Zenodo at https://doi.org/10.5281/zenodo.6524101, Ref. 43.

SOFTWARE USED

The VASP suite with the projector augmented wave (PAW) method and the vdW-df-cx exchange correlation (XC)-functional was used for the total energy calculations and structure relaxations. The GPAW package with linear combination of atomic orbitals (LCAO) basis sets and the LCAO-RT-TDDFT implementation was used for the RT-TDDFT calculations. The ASE library was used for constructing and manipulating atomic structures. The NumPy, SciPy and Matplotlib Python packages and the VMD software were used for processing and plotting data. The Snakemake package was used for managing the calculation workflow.

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Appendix A: Methodology

In the limit of weak perturbation, the system response can be assumed to be linear. This means that the Fourier transform of the response at one particular frequency depends only on the Fourier transform of the perturbation at the same frequency. The response to one time-dependent perturbation can be retrieved knowing the response to another perturbation. We use this property in RT-TDDFT to compute optical spectra (Sect. A 1) and model carrier generation in arbitrary electric fields (Sect. A 2). The geometrical configurations of the systems we studied are presented in Sect. A 3 and computational details including density functional theory (DFT) and RT-TDDFT parameter values in Sect. A 4. For simplicity we adopt Hartree atomic units in this section.

1. Plasmonic response in the $\delta$-kick technique

In the $\delta$-kick technique the time-dependent external potential is set to a kick in the $z$-direction of strength $K_z$ and the system is allowed to evolve in time.

\[
v_{\text{ext}}(r, t) = K_z \delta(t), \tag{A1}\]

We define the induced density due to the $\delta$-kick $\delta n_{\text{kick}}(r, t) = n_{\text{kick}}(r, t) - n(r, 0)$ and the induced dipole moment in the $z$-direction as

\[
\delta \mu_z(t) = \mu_z^{\text{kick}}(t) - \mu_z(0) = \int \, dr \, \delta n_{\text{kick}}(r,t)z. \tag{A2}\]

The optical spectrum in the $z$ direction can then be expressed via the dipole strength function

\[
S_z(\omega) = -\frac{2\omega}{\pi} \text{Im} \left[ \frac{\mu_z(\omega)}{K_z} \right], \tag{A3}\]

where $\mu_z(\omega)$ is the Fourier transform of $\mu_z(t)$.

2. Carrier generation in the $\delta$-kick technique

In KS-RT-TDDFT the KS density operator

\[
\rho(t) = \sum_k |\phi_k(t)\rangle f_k \langle \phi_k(t)| \tag{A4}\]
contains all information about the system. Here, $\phi_k(t)$ are the KS wave functions at time $t$ and $f_k$ their ground state occupation numbers. In practice, the operator is expressed as the KS density matrix in the basis of ground state wave functions $\ket{\phi_k(0)} = \ket{\phi_k(0)}$

$$\rho_{nn'}(t) = \braket{\phi_n(0)}{\rho(t)}{\phi_{n'}(0)} = \sum_k \braket{\phi_n(0)}{\phi_k(t)}{f_k} \braket{\phi_k(t)}{\phi_{n'}(0)}.$$  \hspace{1cm} (A5)

$$\rho_{nn'}(t) = \frac{1}{K_z} \rho_{nn'}^{\text{kick}}(\omega) \mathcal{E}_z(\omega).$$ \hspace{1cm} (A7)

Here, functions of $\omega$ are Fourier transforms of the corresponding time-dependent quantities, and we have constrained ourselves to fields where the $z$-component $\mathcal{E}_z$ is the only non-zero component of $\mathcal{E}$. By the convolution theorem Eq. A7 is equivalent to

$$\rho_{nn'}(t) = \frac{1}{K_z} \int_0^\infty d\tau \rho_{nn'}^{\text{kick}}(\tau) \mathcal{E}_z(t - \tau).$$ \hspace{1cm} (A8)

In linear response we can express the KS density matrix $\rho_{nn'}^{\text{kick}}(t)$ corresponding to an arbitrary time-dependent field $\mathcal{E}(t)$ in terms of the KS density matrix $\rho_{nn'}^{\text{kick}}(t)$ due to the $\delta$-kick

$$\rho_{nn'}^{\text{kick}}(\omega) = \frac{1}{K_z} \rho_{nn'}^{\text{kick}}(\omega) \mathcal{E}_z(\omega).$$

To compute the distributions of generated carriers we follow the method of Ref. 19, where expressions that include second-order corrections to the density matrix are derived. For notational convenience (see Supplementary Note 2 of Ref. 19), we introduce the notation

$$q_{ia}(t) = 2 \text{Re} \delta \rho_{ia}(t)/\sqrt{2(f_i - f_a)}$$ \hspace{1cm} (A9)

$$p_{ia}(t) = -2 \text{Im} \delta \rho_{ia}(t)/\sqrt{2(f_i - f_a)},$$ \hspace{1cm} (A10)

which is well-defined for matrix elements corresponding to occupied ($i$)–unoccupied ($a$) pairs, $f_i > f_a$. Only these occupied–unoccupied pairs are needed to construct the observables of interest.

The probability that a hole (electron) has been generated at time $t$ in state $i$ ($a$) is

$$P^h_i(t) = \sum_a \frac{1}{2} \left[ q_{ia}(t) + p_{ia}(t) \right]$$ \hspace{1cm} (A11)

$$P^e_a(t) = \sum_i \frac{1}{2} \left[ q_{ai}(t) + p_{ai}(t) \right].$$ \hspace{1cm} (A12)

The sum of generated carriers is the same for both types

$$N_{\text{carriers}}(t) = \sum_i P^h_i(t) = \sum_a P^e_a(t).$$ \hspace{1cm} (A13)

Note that integrating Eq. A14 and Eq. A15 over the entire space yields the number density of carriers $\int d\mathbf{r} P^{e/h}(r, t) = N_{\text{carriers}}(t)$. Further, we construct spatio-energetic probability density contributions

$$P^h_i(\varepsilon, r, t) = \frac{1}{2} \sum_{ai'} \left( q_{ia} q_{ia'} + p_{ia} p_{ia'} \right) \psi_i^{(0)}(r) \psi_{i'}^{(0)}(r) \delta(\varepsilon - \varepsilon_i)$$ \hspace{1cm} (A16)

$$P^e_a(\varepsilon, r, t) = \frac{1}{2} \sum_{ia'} \left( q_{ai} q_{ai'} + p_{ai} p_{ai'} \right) \psi_i^{(0)}(r) \psi_{a'}^{(0)}(r) \delta(\varepsilon - \varepsilon_a).$$ \hspace{1cm} (A17)

The $\delta$-functions in energy are in practice approximated by a Gaussian $(2\pi\sigma^2)^{-1/2} \exp(-\varepsilon^2/2\sigma^2)$ with width $\sigma = 0.07$ eV. There is no unique definition for the simultaneous decomposition in time and energy but we obtain consistent results (Fig. S10) with different variants of the former expressions. Note that in contrast to Ref. 19 we include the summation of non-degenerate $ii'$ and $aa'$ which has significant implications in the NP+molecule system (Fig. S10).

In this work, we calculate the fraction of generated carriers in particular regions, i.e., the Voronoi region of
the molecule or the Voronoi region of a particular atomic site

\[
P_{\text{h,region}}(t) = \int_{\text{region}} d\mathbf{r} P_{h}(\mathbf{r}, t) / N_{\text{carriers}}(t) \quad (A18)
\]

\[
P_{\text{e,region}}(t) = \int_{\text{region}} d\mathbf{r} P_{e}(\mathbf{r}, t) / N_{\text{carriers}}(t). \quad (A19)
\]

Similarly, we calculate the energetic distribution in a particular region

\[
P_{\text{h,region}}(\varepsilon, t) = \int_{\text{region}} d\mathbf{r} P_{h}(\varepsilon, \mathbf{r}, t) \quad (A20)
\]

\[
P_{\text{e,region}}(\varepsilon, t) = \int_{\text{region}} d\mathbf{r} P_{e}(\varepsilon, \mathbf{r}, t). \quad (A21)
\]

3. Geometry of atomic structures

In this work we study the regular truncated octahedron (RTO)-shaped Ag$_{201}$, Au$_{201}$, and Cu$_{201}$ NPs. The RTO shape is consistent with an unstrained fcc lattice that has been truncated so that it has eight \{111\} surfaces and six \{100\} surfaces. We identify four molecular adsorption sites on the NP. On the (111) surface we consider the center on-top site and its nearest fcc site (Fig. 1). We also consider the hollow site closest to the center of the (100) face, and the corner site between a \{100\} and two \{111\} surfaces. In each site the immediate environment of the molecule is different; it has one nearest-neighbor metal atom for the (111) on-top and corner sites, three for the (111) fcc site and four for the (100) hollow site.

We place a CO molecule (C facing the metal) near each site and find minimum energy configurations by allowing all metal and molecule atoms to relax. In the relaxed configurations the bond length and NP-molecule distance are thus different for each site.

We study the distance dependence by rigidly shifting the molecule from the adsorbed configuration, i.e., without changing the CO bond length or the positions of the metal atoms. The shift is performed along a line perpendicular to the respective surface for the (111) and (100) sites and along the line through the opposing corner site for the corner site. We note that at long separations such rigidly shifted configurations are relatively high in energy. Specifically, at long distances the minimum energy configuration would be a molecule with the bond length of bare CO and a fully relaxed bare NP. In general, finding such minimum energy configurations under a distance constraint is a highly multidimensional problem. We therefore limit our discussion to rigid translations of the molecule, without compromising our conclusions (Fig. S11).

4. Computational details

The VASP\textsuperscript{44–46} suite was used for all structure relaxations and total energy calculations. Ground state energies were computed using a plane-wave basis set, the PAW\textsuperscript{47,48} method, and the vdW-df-cx\textsuperscript{49,50,52,64} XC-functional. The plane wave cutoff 500 eV was used. We used a Gaussian occupation number smearing scheme with the parameter 0.1 eV.

Structure relaxations were performed using the conjugate gradient relaxation method implemented in VASP. Relaxation was stopped when the maximal force on any atom fell below 0.015 eV Å\textsuperscript{-1}. relaxations were performed for each NP separately to obtain relaxed bare NP structures. Additionally for each NP and each adsorption site the NP+molecule system was relaxed, with all atoms allowed to move.

The open-source GPAW\textsuperscript{53,54} code package was used for all calculations of plasmonic response and carrier generation. Kohn-Sham DFT (KS-DFT) ground state calculations were performed within the PAW\textsuperscript{48} formalism using LCAO basis sets;\textsuperscript{55} the double-\(\zeta\) polarized (dzp) basis set was used for C and O, and the \(p\)valence\textsuperscript{56} basis set, which is optimized to represent bound unoccupied states, for Ag, Au and Cu. The Gritsenko-van Leeuwen-van Lenthe-Baerends-solid-correlation (GLLB-sc)\textsuperscript{52,65} XC functional was used. A simulation cell of 32 Å × 32 Å × 38.4 Å was used to represent wave functions, XC, and Coulomb potentials, with a grid spacing of 0.2 Å for wave functions and 0.1 Å for potentials. The Coulomb potential was represented in numerical form on the grid, with an additional analytic moment correction\textsuperscript{66} centered at the NP. Fermi-Dirac occupation number smearing with width 0.05 eV was used for all calculations, except for the Cu corner site for distances ≥ 2.7 Å and for Au (111) on-top distances between 3.1 and 3.7 Å. The effect of different occupation number smearing is negligible for our results (Fig. S13). The self-consistent loop was stopped when the integral of the difference between two subsequent densities was less than 1 × 10\textsuperscript{-8}. Pulay\textsuperscript{67}-mixing was used to accelerate the ground state convergence.

The LCAO-RT-TDDFT implementation\textsuperscript{56} in GPAW was used for the RT-TDDFT calculations. A \(\delta\)-kick strength of \(K_z = 0.51 \times 10^{-4} \text{mV Å}^{-1}\) was used. The time propagation was done in steps of 10 fs for a total length of 30 fs using the adiabatic GLLB-sc kernel. We computed carrier generation for an external electric field corresponding to an ultra-short Gaussian laser pulse

\[
\mathcal{E}_\varepsilon(t) = \mathcal{E}_0 \cos(\omega_0 t) \exp\left(- (t - t_0)^2 / \tau_0^2 \right) \quad (A22)
\]

of frequency \(\omega\), strength \(\mathcal{E}_0 = 51 \text{ mV Å}^{-1}\), peak time \(t_0 = 10\) fs, and duration \(\tau_0 = 3.0\) fs.

We computed the total DOS as

\[
\sum_k \delta(\varepsilon - \varepsilon_k) \quad (A23)
\]

and the molecular PDOS as

\[
\sum_k \delta(\varepsilon - \varepsilon_k) \int_{\text{molecule}} \left| \phi_k^{(0)}(\mathbf{r}) \right|^2 d\mathbf{r}, \quad (A24)
\]
where $\varepsilon_k$ and $\phi_k^{(0)}(r)$ are the KS eigenvalues and wave functions. For visualization, the $\delta$-functions in energy were replaced by a Gaussian $(2\pi\sigma^2)^{-1/2}\exp(-\varepsilon^2/2\sigma^2)$ with width $\sigma = 0.05$ eV.

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