Nonlinear Plasmonic Photoelectron Response of Ag(111)

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Photons can excite collective and single-particle excitations in metals; the collective plasmonic excitations are of keen interest in physics, chemistry, optics, and nanotechnology because they enhance coupling of electromagnetic energy and can drive nonlinear processes in electronic materials, particularly where their dielectric function ε(ω) approaches zero. We investigate the nonlinear angle-resolved two-photon photoemission (2PP) spectroscopy of the Ag(111) surface through the ε(ω) near-zero region. In addition to the Einsteinian single-particle photoemission, the 2PP spectra report unequivocal signatures of nonlocal dielectric, plasmonically enhanced, excitation processes.

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The complex dielectric tensor ε(ω) defines how electrons in a metal experience an optical field and participate in the nonlinear electro-optic response. The epsilon near zero (ENZ); Re[ε(ω)] = 0] condition defines the bulk plasmon frequency ωp, and marks an abrupt change in light-matter interactions in solids [1–10]. The ENZ condition is intrinsic to metals [11–14], but also defines the optical properties of doped semiconductors [15], optical phonons, and metamaterials [16,17]; it designates a frequency region where the reflectivity drops to a minimum and the dielectric response at surfaces is nonlocal [11,18–20], and dominantly nonlinear [15,16,21,22]. Below ENZ (Re[ε(ω)] < 0), the screening in metals occurs mainly through a virtual plasmonic response, and is manifested by high reflectivity; for Re[ε(ω)] ≥ 0, ℏω ≥ ℏωp, the screening by free electrons becomes ineffective [11,18–20,23,24]. Moreover, at ENZ, Im[ε(ω)] rises stepwise [14], because for ℏω ≥ ℏωp, the transverse optical field penetrates a metal as the longitudinal bulk plasmon mode through the nonlocal dielectric response [8,9,11,18,19,25].

Silver is a broadly investigated metal with spectacular optical properties that derive from its plasmonic response. Its interband transitions modify the dielectric response from that of a free electron metal, by reducing its plasmon frequency from ~9 eV, expected from its free electron density, to ℏωp = 3.8–3.9 eV [12,14]. Although the bulk plasmon is intrinsic, the related morphology derived surface plasmon polariton (SPP) and Mie plasmon modes are intensely investigated for their applications ranging from quantum computing to energy and medicine [3,26–28]. While these optical responses have mustered much interest, the fundamental bulk plasmon response of crystalline Ag has hardly been explored by electronic, photoemission, and nonlinear-optical spectroscopy [21]. Thus, the collective nonlinear electronic response of single crystal Ag(111) sets a benchmark for understanding and manipulating the optical responses of more complex metals [17,18,28–30].

The frequency dependent optical response of a solid is expressed in its photoelectron spectra [24,31,32]. Although angle-resolved photoemission records energy and momentum distributions of single electrons [33], it also communicates on the many-body responses. For example, when photons suddenly expose Coulomb fields [7,34–36], the screening response causes plasmon satellites to decorate the main photoemission peaks [33]. Time resolving the primary photoemission and its collective echoes, however, requires attosecond time resolution [37]. In free electron Al and Be metals, the modulation of spectral intensities when ℏω is scanned through the ENZ region reveals the plasmonic participation in one-photon photoemission (1PP) [11,24,31,38]. The work function of Ag (Φ ~ 4.5 eV), however, blocks observation of such responses through ENZ (~3.9 eV).

Two-photon photoemission (2PP) spectroscopy may circumvent this impediment, because scanning of the excitation light through the ENZ region enables the nonlinearly excited electrons to communicate information on their plasmonic origin. Although Ag(111) and Ag(100) surfaces have been extensively investigated primarily by two-color (UV and IR) 2PP spectroscopy [39–45], their plasmonic optical responses have not been addressed. Here, we report how the collective plasmonic responses appear in the nonlinear 2PP spectra of Ag(111). In addition to Einsteinian processes, where optical fields excite single particles, we find that they also excite the plasmonic modes leading to novel spectroscopic features and optical excitation beyond the single-particle band structure of Ag.

We measure angle-resolved 2PP spectra of Ag(111) surface at 90 K, excited by a tunable noncollinear optical parametric amplifier (NOPA) pumped by a 1 MHz repetition...
rate Clark MXR Impulse laser. Frequency doubling of the NOPA output produces excitation pulses of $\approx 20-30$ fs duration, in the $2.6 < \hbar \omega < 4.5$ eV range, with an average power of $1-10$ mW; $p$-polarized light incident at 45° with respect to the surface normal excites the surface [29,30,46]. Figures 1 and 2, respectively, show photoelectron energy- and $k_{\parallel}$-momentum-resolved 2PP spectra for different $\hbar \omega$ and their profiles for normal emission ($k_{\parallel} = 0$ Å$^{-1}$); Fig. 3 plots the photoelectron energies, $E_f$, relative to the Fermi energy, $E_F$, and intensities vs $\hbar \omega$ for the spectral features.

The $E_f(k_{\parallel})$ resolved 2PP spectra for excitation below [Figs. 1(a), 1(b)] and above [Figs. 1(c), 1(d)] ENZ are dramatically different. For $\hbar \omega < \hbar \omega_p$, a two-photon resonant transition between the lower $L_{sp}$ and the upper $U_{sp}$ bulk $sp$ bands [SP transition; see the energy level and excitation diagram for Ag(111) in Fig. 2(a)] appears with far higher intensity than signal from the nonresonant two-photon excitation of the Shockley surface (SS) state [30]. The $k_{\parallel}$ ranges of SS and the SP transition are limited, respectively, by their dispersions to above $\hbar \omega_p$ [Figs. 1(c), 2(b)]. Notably, above $\hbar \omega_p$, the surface states dominate the 2PP spectra. The $E_f$ values of the SS and IP peaks vary with $2\hbar \omega$ and $\hbar \omega$, respectively [Fig. 3(a)], as expected for the initial and intermediate states in 2PP spectra [39]. The pronounced intensity variation of the bulk SP transition and appearance of a new spectral feature at $E_f \approx 7.75$ eV, however, herald plasmonic responses of the Ag(111) surface (Figs. 1–3).

First, we consider the nonlinear coupling of the bulk $sp$ bands of Ag by a two-photon excitation, which can be excited in the entire investigated $\hbar \omega$ range. The SP transition is the dominant spectroscopic feature in 2PP spectra for $\hbar \omega < \hbar \omega_p$, with a maximum for $\hbar \omega \approx 3.4-3.5$ eV, to vanishing above $\hbar \omega_p$ [Fig. 3(b)]. This drastic intensity variation cannot be attributed to transition moments, because in linear 1PP spectra for $\hbar \omega = 6-10$ eV, the SP transition varies by only $\sim 50\%$ with respect to the SS photoemission [47]. Instead, we attribute its intensity variation to screening of the surface fields, to which 2PP, being proportional to $E(\omega)^4$, is exceptionally sensitive. The near surface field in a metal below $\hbar \omega_p$ is defined by the external field and the multipole plasmon (MP) nonlocal screening response [13,24,31,48]. The MP resonance of Ag(111) has been reported at $\hbar \omega_{MP} = 3.74$ eV in EELS spectra by Rocca and co-workers [49], but it is expected to enhance the near-surface fields over a broad frequency range [1,2,13]. Our finding of the strong SP transition intensity modulation is consistent with the near-surface field enhancement by the MP screening.

The MP field enhancement can also be confirmed by comparing 2PP spectra of Cu(111) and Ag(111) surfaces; both metals have very similar band structures, electron escape depths, etc., except for their plasmonic responses, which is at a higher frequency and less well defined for Cu [9]. Because Cu(111) experiences less pronounced MP response than Ag(111), its SP transition is barely detected (see Supplemental Material S1 [50] and Ref. [51]).
precipitously decreases towards $\hbar \omega$ above it. The $2\text{PP}$ from SS of Ag(111) is not clear, because our measurements cover a limited range ($\Delta \hbar \omega < 2$ eV), where its intensity is affected by resonance with the $p$-bands as well as surface states (SS, IP). The spectral $k_\parallel = 0$ Å$^{-1}$ profiles from data like in Fig. 1 are normalized at the work function edge; they are shifted vertically by photon energy differences. The main features are labeled in the figure. (c) Expanded 2PP spectra displaying the asymmetric peak at $2\hbar \omega_p \approx 7.75$ eV (highlighted by the brown box), which has a constant $E_f$ for increasing $\hbar \omega$, and cannot be assigned within the single-particle band structure in (a).

The MP response is known to enhance 1PP yields from surface states of free electron metals over a broad energy range ($\Delta \hbar \omega \approx 5$ eV) [24,38,67]. Whether it also affects the 2PP from SS of Ag(111) is not clear, because our measurements cover a limited range ($\Delta \hbar \omega < 2$ eV), where its intensity is affected by resonance with the $n = 1$ IP state, in near coincidence with ENZ.

Next, we consider the spectral feature at $E_f \approx 7.75$ eV $\approx 2\hbar \omega_p$; its characteristics are that it appears only for $\hbar \omega \geq 3.9$ eV with gradually decreasing intensity [Figs. 2(c), 3], its line shape is asymmetric [see Fig. 2(e)], and it disperses over the accessible $k_\parallel$ range. Most significantly, the $E_f$ of the $2\hbar \omega_p$ feature does not increase with $\hbar \omega$.

Giesen et al. reported the same feature in one-color 2PP spectra of Ag(111) excited with a tunable nanosecond laser [39]. A 2PP peak that is independent of $\hbar \omega$ is exceptional; it could signify a two-photon excitation to a final state at a fixed $E_f$, or a process where excitation at $\hbar \omega$ creates a field at $\hbar \omega_p$. The only final state at $E_f \approx 7.75$ eV is the three-dimensional $U_{sp}$ band, but there is no reason for photoemission from $U_{sp}$ to localize at this $E_f$ [cf. band-diagram in Fig. 2(a) and Refs. [32,47,52]]. Instead, Giesen et al. attributed the $E_f \approx 7.75$ eV peak to an Auger process where a pair of electrons in the proximate $n = 1$ IP state scatter deactivating one and causing the other to be photoemitted at their combined energy. Because our laser pulse duration is comparable to the $n = 1$ IP state lifetime [44], and six orders of magnitude shorter than that of Giesen et al., the putative Auger process, which should depend quadratically on the IP state population, is inconsistent with appearing in both experiments with comparable intensity relative to the IP state (Supplemental Material S2 [50]). Moreover, we can also exclude the Auger process by depositing organic molecules onto Ag(111) surface [53], which quenches the SS and IP state signals differently from the $2\hbar \omega_p$ feature, indicating that they are unrelated (Supplemental Material S3 [50]). Instead, we attribute the $2\hbar \omega_p$ feature to decay of two bulk plasmon...
quanta, which can be excited for $\hbar \omega \geq \hbar \omega_p$ and must excite single photoelectrons from $E_F \rightarrow E_F \approx 2 \hbar \omega_p$. We note that a similar $\hbar \omega$-independent, though unassigned, feature has been reported in 2PP spectra of Ag(100) in the 4.60 < $\hbar \omega$ < 4.95 eV range at $E_F \approx 7.9$ eV [68]. Observation of the $2 \hbar \omega_p$ feature on different crystalline planes of Ag can only be consistent with the bulk plasmon excitation, which is the only mode that could depend weakly on the crystal orientation. Also, in EELS spectra of Ag(111) with $>70$ eV electrons, a $2 \hbar \omega_p$ loss peak has been reported at 7.6 eV [69,70], approximately where we detect the $2 \hbar \omega_p$ feature.

Why the $2 \hbar \omega_p$ feature appears at twice the bulk plasmon frequency needs to be addressed. Screening of the transverse $p$-polarized optical field by the nonlocal dielectric response induces a surface charge density, including the longitudinal bulk plasmon, to be excited at the Ag surface. This response induces a surface charge density, including the longitudinal plasmon, which can only be consistent with the bulk plasmon excitation, which is the only mode that could depend weakly on the crystal orientation. Also, in EELS spectra of Ag(111) with $>70$ eV electrons, a $2 \hbar \omega_p$ loss peak has been reported at 7.6 eV [69,70], approximately where we detect the $2 \hbar \omega_p$ feature.

The $2 \hbar \omega_p$ feature appears at twice the bulk plasmon frequency needs to be addressed. Screening of the transverse $p$-polarized optical field by the nonlocal dielectric response induces a surface charge density, including the longitudinal bulk plasmon, to be excited at the Ag surface. This response has been calculated to decrease because the longitudinal plasmon cannot respond sufficiently fast as $\hbar \omega$ is scanned above $\hbar \omega_p$, [11,20], as is observed in our experiment. The bulk plasmon is a polarization field at $\omega_p$ that can act as a secondary source to excite additional $e$-$h$ pairs. The decay of plasmons into single particle excitations is thought to excite electrons from $E_F - \omega_p$ up to $E_F$, to final states from $E_F$ up to $E_F + \omega_p$, with only the density of states determining the hot electron energy distribution [71]. In the 2PP experiment, however, we measure the peak at $E_F = 2 \hbar \omega_p$ where plasmon-excited electrons must have been preferentially excited from initial states near $E_F$. Such a photoemission scenario is unconventional, but has precedent in the constant initial state photoemission spectra of alkali atom covered thin Ag films where $\hbar \omega$ was tuned through ENZ and photoemission was monitored from specific initial states; by using the alkali coverage to reduce the work function photoemission with $\hbar \omega = 1 \hbar \omega_p$ could be observed and found to be enhanced from $E_F$ [32]. In addition, we show in the Supplemental Material S4 (Fig. S5) [50] that the $2 \hbar \omega_p$ feature is strongly sensitive to temperature, implicating the electron occupation discontinuity at $E_F$. We note that single-particle 2PP from $E_F$ at $k_p = 0 \text{ Å}^{-1}$ is not possible, because the band gap of Ag(111) extends from $E - E_F = -0.4$ to 3.9 eV [72]. The SS state just below $E_F$ is also unlikely as the initial state, because (i) its $k_p$-dispersion and occupation range does not match the $2 \hbar \omega_p$ feature [Fig. 2(e)], and (ii) it is quenched more rapidly by molecular adsorption (Fig. S4 [50]). In a many-body process, however, electrons from $E_F$ can be photoemitted at $k_p = 0 \text{ Å}^{-1}$, if multiple particle scattering conserves momentum. The bulk plasmon response involves electron charge-density fluctuations at $E_F$, and thus it may induce photoemission of the same population.

To test our hypotheses and confirm that in the linear response $\omega_p$ decay excites electrons to $E_F \approx 1 \hbar \omega_p$, as has been reported for Na/Ag(100) films [32], we lower the work function of Ag(111) by submonolayer chemisorption of Rb, which only modifies the surface electronic structure of Ag [54]. Indeed, 1PP spectra of Rb/Ag(111) with Hg-lamp excitation ($\hbar \omega \approx 4.86$ eV; Supplemental Material S5, Fig. S6 [50]) reveal that besides the single particle features of Ag(111), a broad peak appears at $E_F \approx 3.7$ eV consistent with the bulk plasmon decay exciting electrons from $E_F$ to $E_F \approx 1 \hbar \omega_p$. Thus, the $2 \hbar \omega_p$ feature of Ag surfaces [39,68] is a robust nonlinear counterpart where two $\hbar \omega_p$ quanta excite single electrons from $E_F$, which is consistent with the previous 1PP spectra of Ag films [32]. This previously unknown mode of bulk plasmon decay warrants further theoretical scrutiny.

We have investigated the nonlinear optical response of the pristine Ag(111) surface in the near UV by tuning the photon energy through the ENZ region. The observed 2PP spectra have contributions from the single particle surface and bulk excitations as well as the collective bulk plasmon response causing emission at $E_F = 2 \hbar \omega_p$. The intensities of surface state 2PP spectra of Ag(111) primarily reflect the IP $\rightarrow$ SS resonance, rather than the nonlocal dielectric ENZ response. By contrast, the two-photon resonant excitation of the SP transition has a pronounced intensity variation that is absent in 1PP spectra. The 2PP process, however, is nonlinear and therefore is enhanced for $\text{Re}[\varepsilon(\omega)] < 0$ through the multipole plasmon resonance. Pfeiffer and co-workers have described a similar scenario for intensification of 2PP by excitation of plasmonic fields in metal nanoparticles [73], and Timm and Bennemann have described how dielectric screening affects the effective fields in nonlinear optical transitions [36]. Consistent with their models, we observe that screening of the optical field by multipole plasmon response strongly modulates the 2PP intensities of bulk transitions below $\hbar \omega_p$. Furthermore, above the bulk plasmon resonance, we find that the longitudinal bulk plasmon mode is excited and a two-quantum decay unexpectedly generates a spectroscopic feature, which appears only for $\hbar \omega \geq \hbar \omega_p$, where photoelectrons from $E_F$ are excited to $E_F = 2 \hbar \omega_p$. Similar nonlinear plasmon-induced photoemission has recently been invoked in space- and time-resolved photoemission electron microscopy [74] of plasmonic nanostructures up to fifth order of the plasmon field when exciting Au at moderate powers with an ultrafast Ti:sapphire laser oscillator [75]. Therefore, we find signatures of non-Einsteinian photoemission where photoelectron distributions are not defined only by $\hbar \omega$ of the external optical field and the single-particle band structures, but also include contributions from the intermediate nonlocal collective plasmonic responses that are particularly strong in the ENZ region. The electronic screening responses can strongly modulate the near-surface fields, as is evident from the nonlinear photoemission intensities, and even generate photoemission spectroscopic features beyond the single-particle band structures of metals that imply previously unknown
propensity for bulk plasmons to decay by excitation of hot electrons from \( E_F \). Our findings demonstrate how the collective nonlocal dielectric surface responses enhance the surface fields in the ENZ region and thereby affect the nonlinear optical processes. Particularly, the plasmonic excitation of hot electrons from \( E_F \), benefits the energy harvesting in plasmonically driven processes on metals [3,6,27].

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See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.123.017404 for 2PP spectroscopy of Cu(111), a comparison of 2PP and 3PP spectroscopy of Ag(111), PTCDA/Ag(111)-coverage dependent 2PP spectra, temperature dependent 2PP spectra of Ag(111), and Rb/Ag(111)-coverage dependent 1PP spectra. The Supplemental Material includes Refs. [9,12,30,32,39,44,45,47,51–67].

Supplemental Material

The nonlinear plasmonic photoelectron response of Ag(111)

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**Figure S1** | (a) $E_f(k||)$-distribution of Cu(111) as excited with 3.41 eV photons, the spectrum is composed of the coherent non-resonant 2-photon SS state excitation and the resonant SP transition [the excitation diagram as a function of $k_\perp$ is given in (c)]. (b) Line profiles taken at $k_\parallel = 0$ in a photon energy range between 2.88 and 4.22 eV. The spectra are normalized at the work function edge and shifted on the vertical axis by $\Delta \hbar \omega$.

**Figure S2** | Energy- and $k_\parallel$-resolved 2PP spectra of the Cu(111) surface for photon energies between 3.90 and 4.62 eV, each color table is scaled independently. (a) For $h\omega = 3.90$ eV, the SS state as well as the d-band are detected. (b) When increasing the photon energy from 4.2 to 4.5 eV, an intensity enhancement due to the $n = 1$ IP $\leftrightarrow$ SS resonance is observed for different $k_\parallel$, because of their different dispersions. (c) Line profiles of Cu(111) spectra taken at $k_\parallel = 0$; the spectra are normalized at the work function edge and shifted on the vertical axis by $\Delta \hbar \omega$. The 2PP spectra of Cu probe the very similar single-particle band structure, but do not exhibit plasmonic responses found for Ag(111). (d) Excitation diagram for $k_\parallel = 0$, 2PP of the SS state at $h\omega = 3.90$ eV (blue) as well 2PP in the IP $\leftrightarrow$ SS resonance (cyan) are indicated by the arrows.
The projected surface band structures of Ag(111) and Cu(111) are qualitatively similar: The SS state as well as the $n = 1$ IP state are within their band gaps while the higher lying IP states ($n \geq 2$) are resonant with the $U_{\text{sp}}$-band [1-6]. Besides minor differences in binding energies, $k_{||}$-dispersions and electron dynamics of the electronic states, both surfaces mainly differ in their dielectric functions and thus, most pertinently, their bulk plasmon frequencies [7]. While for Ag, the bulk plasmon frequency is smaller than the work function ($\Phi \approx 4.5$ eV vs. $h\omega_p \approx 3.9$ eV), the bulk plasmon frequency of Cu is not well-defined, but has been estimated to be in $\sim 20$ eV range [7,8].

In Fig. S1 and Fig. S2, we show 2PP spectroscopy of the clean Cu(111) surface as excited in a photon energy range of $2.88 \text{ eV} < h\omega < 4.62 \text{ eV}$ where we can contrast the characteristics of both the SP transition as well as the IP $\rightarrow$ SS resonance, with those of Ag(111).

**sp-Band intensity**

In Fig. S1(a), we show an $E(k_{||})$ distribution of photoelectrons recorded in 2PP from Cu(111) upon excitation with $h\omega = 3.41$ eV photons. The SP transition and the SS state are detected in resonant and non-resonant coherent 2-photon excitation, respectively [the excitation diagram as a function of $k_\perp$ is presented in Fig. S1(c)]. In Fig. S1(b), we show 2PP spectra for $k_{||} = 0$ for $h\omega = 2.88$ to 4.22 eV, which are in agreement with literature [2]. We first focus on the 2-photon SP transition, which has the following properties: (i) it is detected in a narrow photon energy range, $3.3 \text{ eV} < h\omega < 3.5 \text{ eV}$; (ii) it has a parabolic $k_{||}$-dispersion; (iii) it is superimposed on d-band photoemission for $h\omega > 3.5 \text{ eV}$; and (iv) its photoemission intensity is substantially weaker than that of the SS state.

Although Cu(111) and Ag(111) have similar single particle band structures, their SP transitions appear with dramatically different relative intensities. Whereas for Cu(111) the SP transition is
hardly detected in 2PP, for Ag(111) it dominates 2PP spectra for $\hbar \omega < 3.9$ eV [Fig. 1(a,b), Fig. 2(b), Fig. 3]. This difference can be attributed to their dielectric functions: as outlined in the main text, for Ag(111), the resonant 2-photon SP transition gains intensity by enhancement of the local field from the multipole surface plasmon response. By contrast, on Cu(111), ENZ and thus strong plasmonic field enhancements cannot be expected in the energy range where the SP transition is observed ($3.3 \, \text{eV} < \hbar \omega < 3.5 \, \text{eV}$), as these are expected at a much higher energy [7]. The SP transition for Ag(111) has been observed in 1PP for $\hbar \omega \sim 6-10$ eV, where a plasmonic field enhancement is not expected [9]; by contrast to 2PP spectra, in 1PP spectra, the SP transition is not strongly $\hbar \omega$ dependent, and it strength is comparable or weaker than that of SS. We thus conclude, that the strong $\hbar \omega$ dependence of the 2-photon SP transition in Ag(111) can be attributed to the local field enhancement due to the plasmonic screening of the optical field below $\hbar \omega_p$.

**IP ↔ SS resonance**

In Fig. S2, we show 2PP spectra of Cu(111) when tuning the photon energy through the SS ↔ $n = 1$ IP resonance, the photoemission intensity is enhanced for selected $k_\parallel$ due to the different $k_\parallel$-dispersions of the coupled states. Most relevant for this work is the following observation: When comparing the photon energy dependent 2PP data of Cu(111) in Fig. S2 with the 2PP data of Ag(111) in Fig. 1 and Fig. 2 of the main text, the surface states behave similarly, i.e., their photon energy dependent spectroscopy is mainly dominated by the SS ↔ IP resonance. Because for Cu(111) surface, plasmonic effects are not expected [7,8], the similar behavior of the same transition on Ag(111) suggest that plasmonic effects do not strongly affect its surface state 2PP processes.
**S2 2PP and 3PP spectroscopy of Ag(111)**

![Figure S3](image)

**Figure S3** | Energy- and $k_{||}$-resolved (a) 2PP and (b) 3PP spectra when exciting with $\hbar \omega = 4.22$ eV and $\hbar \omega = 2.12$ eV, respectively (the color tables are scaled independently). In (b), the color scale is enhanced by a factor 1000 for $E_F > 7.3$ eV to show the ATP signal. (c) Line profiles taken at $k_{||} = 0$ are shown on a logarithmic scale of intensity. (d) Excitation diagram at $k_{||} = 0$, the cyan and the orange arrows indicate the 2-photon and 3-photon excitation processes from SS, respectively; the dashed arrow indicates ATP. For $\hbar \omega = 4.22$ eV, the $n = 1$ IP state, the SS state as well as the $2\hbar \omega_p$-feature are resolved in 2PP. For $\hbar \omega = 2.12$ eV, the $n = 1$ IP state, the SS state as well as the $n = 1$ IP state in ATP are observed, respectively.

In 1985, Giesen *et al.* [10] reported 2PP spectroscopy of Ag(111) using tunable nanosecond dye laser pulse excitation and reported similar spectroscopic features as discussed in this Letter. As we outline in the following, we do not concur with some of their assignments. Giesen *et al.* did not consider the role of plasmonic excitations, but mainly the resonance condition between the SS state and the $n = 1$ IP states when exciting with $\hbar \omega \geq \hbar \omega_p \approx 3.9$ eV photons.

Specifically, Giesen *et al.* assigned the $2\hbar \omega_p$-feature to energy-pooling, an Auger process where a large density of electrons excited to the $n=1$ IP state can decay by impact ionization where two IP state electrons scatter causing one to decay to $E_F$ and the other to acquire the initial energy of both.
This would cause the ionized electron to appear at twice the \( n = 1 \) IP state energy (at \( k_{||}=0 \) Å\(^{-1}\)), which is nearly degenerate with \( E_f \) of the \( 2\hbar\omega_p \)-feature. We can exclude the Auger-like decay process based on the following arguments and experimental results. (i) Energy pooling, as a two-electron process, should be strongly dependent on the \( n = 1 \) IP state population. In our work, we excite the IP state with femtosecond laser pulses, whereas Giesen et al. worked with nanosecond lasers. The IP state population should depend on both the laser pulse duration and the IP state lifetime. Because \( n = 1 \) IP state lifetime is \( \approx 30 \) fs [4], which was not known to Giesen et al., the energy pooling process should be far more efficient with our fs excitation source, but this is not the case. Because the \( 2\hbar\omega_p \)-feature is detected with qualitatively comparable relative intensity to the \( n = 1 \) IP state, we can rule out energy pooling, as being responsible for the \( 2\hbar\omega_p \)-feature. (ii) In Fig. S3, we show the \( n = 1 \) IP state region in 2PP spectra of Ag(111) excited with \( \hbar\omega = 4.22 \) eV together with a three-photon photoemission (3PP) excited with \( \hbar\omega = 2.12 \) eV. As discussed in the main text, for \( \hbar\omega \geq \hbar\omega_p \), the \( 2\hbar\omega_p \)-feature is clearly resolved and appears in the 2PP spectrum. Energy-pooling should not depend on the excitation pathway, i.e. whether the IP state is excited by 1- or 2-photons and thus it should be observed when exciting with \( \hbar\omega = 2.12 \) eV, because we can efficiently populate the \( n = 1 \) IP state through a two-photon process. As can be clearly seen in Fig. S3(b) and Fig. S3(c), however, although the \( n = 1 \) IP state is strongly populated by two-photon excitation with \( \hbar\omega = 2.12 \) eV, the \( 2\hbar\omega_p \)-feature is not observed when \( \hbar\omega < \hbar\omega_p \); therefore, the assignment of energy pooling to the \( 2\hbar\omega_p \)-feature can be excluded. (iii) For energy pooling to be \( \hbar\omega \) independent, energy relaxation must occur from \( k_{||} \neq 0 \) Å\(^{-1}\) states to \( k_{||}=0 \) Å\(^{-1}\) before the Auger process occurs. Such fast intraband relaxation within IP states is not observed. (iv) If energy pooling occurs in Ag(111), it could also occur in Cu(111); there is no evidence for that in, for example, Fig. S2. The argument against energy pooling is further supported
by observation of above-threshold photoemission (ATP) of the IP state with $h\omega = 2.12$ eV: The ATP signal is typically a factor 10 to $10^3$ weaker than the lower-order photoemission process [11-13]. Because our experiment is sensitive to ATP electrons, as from the $n = 1$ IP state, it should also be sensitive to electrons from energy-pooling. Further arguments are given in section S3.
S3 Molecular–coverage dependent 2PP spectra of Ag(111)

**Figure S4** | 2PP spectra for different PTCDA coverages \((\hbar\omega = 4.58 \text{ eV}, k_{||} = 0, \text{300 K})\). The spectra are normalized at the work function edge. In the inset, the signal is normalized on the \(n = 1\) IP state intensity and offset by an arbitrary amount on the vertical axis. With increasing PTCDA coverage, the initially occupied SS state disappears and the unoccupied Shockley-type metal-organic interface state (IS) is formed. The SS state intensity drops significantly faster than for the \(2\hbar\omega_{p}\)-feature.

The electronic structure and the electron dynamics at molecule-metal interfaces are intensively studied with 2PP [14,15]. Here, we make use of 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) adsorption on Ag(111) in order to eliminate the possibility of \(n = 1\) IP \(\rightarrow\) SS state resonance from contributing to the \(2\hbar\omega_{p}\)-feature, and thus to exclude the Auger decay process proposed by Giesen *et al.* [10].

Upon adsorption of a few molecular layers of PTCDA on Ag(111), the SS of the clean Ag(111)
surface becomes an unoccupied Shockley-type resonance of the metal-organic interface [15,16]. In Fig. S4, we show PTCDA coverage dependent 2PP data ($h\omega = 4.58$ eV, $k_{||} = 0$, 300 K). With increasing coverage, the Shockley-type interface state (IS) is formed and detected in 2PP, while the intensity of SS state of the clean surface drops significantly. For highest coverage ($\geq$ 1ML), the SS state signal has disappeared, because it has become the IS state [16]; however, the $2h\omega_p$-feature is still visible in the data. The $n = 1$ IP state peak is still observable, but that is because the IP state can exist on the organic/vacuum interface. We make use of the coverage dependent 2PP data to conclude that the SS state and the $2h\omega_p$-feature are independent photoemission spectral features. Most importantly, the Auger process should have a quadratic dependence on the IP state density. Quenching the IP state 2PP signal should quench the Auger process much faster, which is not observed. These observations strongly contradict the attribution of the $2h\omega_p$-feature to an Auger decay process proposed in Ref. [10].
Figure S5 | Temperature dependent 2PP spectra taken with 4.22 eV photons ($k_\parallel = 0$). The $n = 1$ IP state and the SS state as well as the $2\hbar \omega_p$-feature are resolved at 90 (blue) and 300 K (green) sample temperatures; these features become sharper and more intense at 90 K. The spectra are normalized at the work function edge. In the inset, the signal is normalized on the $n = 1$ IP state intensity.

To further determine origin of the $2\hbar \omega_p \approx 7.75$ eV feature, we investigate its temperature dependence in 2PP spectra. The motivation for such measurement is that if the emission involves states close to $E_F$, then the 2PP spectrum should be sensitive to temperature because it will be influenced by the Fermi-Dirac distribution, and electron-phonon interaction. By contrast, if it involves states far from $E_F$, the spectra should be independent of temperature, because electron occupations will be 0 or 1, and the lifetimes will be determined by electron-electron interaction. One caveat is that long lived surface states far from $E_F$ could also be significantly influenced by electron-phonon interaction [17].
Figure S5 shows temperature dependent 2PP data of Ag(111) excited with 4.22 eV photons ($k_\parallel = 0 \ \text{Å}^{-1}$). For 90 and 300 K sample temperature, the $n = 1$ IP and the SS states as well as the $2\hbar\omega_p$-feature are resolved, however, as the spectra clearly indicate, both the $2\hbar\omega_p$-feature as well as the $n = 1$ IP state are temperature dependent: At 300 K, their linewidths are significantly broadened as would be expected for electrons, which are excited from the Fermi level or sensitive to electron-phonon interaction. The broader width and larger temperature sensitivity of the $2\hbar\omega_p$-feature may be related to the canonical $4k_B T$ (100 meV at 300 K) width of Fermi-Dirac distribution.
S5 Rb/Ag(111) - coverage dependent 1PP spectra excited with an Hg-lamp

**Figure S6** | (a) $E(k_\parallel)$-distributions as excited with a Hg-lamp ($\hbar\omega = 4.86$ eV) of the pristine Ag(111) (left) and the Rb/Ag(111) (right) surface. The photoemission spectral elements are labelled in the figure. (b) Energy-resolved 1PP spectra of Rb/Ag(111) for $k_\parallel = 0$; the Rb coverage is increased continuously to lower the work function. For the pristine Ag(111) surface (black spectrum), the SS state is resolved. As the work function decreases from $\approx 4.5$ eV (clean surface, black spectrum) to $\approx 3.1$ eV (purple spectrum), the resonant 1-photon transition between the lower, $L_{sp}$, and the upper, $U_{sp}$, sp-band becomes apparent at a final state energy of $E_f \approx 4.2$ eV. At a final state energy of $E_f \approx 3.7$ eV $= \hbar\omega_p$, electrons as emitted by the decay of one bulk plasmon are detected. The $1\hbar\omega_p$-features has a broad line shape in energy and momentum space. (c) $k_\parallel$-resolved band structure in $\Gamma$-L direction indicates the 1-photon SP transition (dashed line) and SS state excitation (solid line) ($E_{vac} \approx 3.1$ eV).
We report the detection of electrons that appear to be excited by decay of bulk plasmons in Ag(111). For the pristine Ag(111) surface, single particle electrons excited by one bulk plasmon ($\hbar\omega_p \approx 3.8-3.9$ eV) do not have sufficient energy to overcome the work function to be photoemitted. Instead, as discussed in main text, in 2PP electrons excited by decay of two bulk plasmons are detected at a final state energy of $2\hbar\omega_p \approx 7.75$ eV. If this excitation pathway is feasible, we also might expect electrons to be excited to $E_f = 1\hbar\omega_p \approx 3.8$ eV, and be emitted if the work function were sufficiently low.

To test this hypotheses, we decrease the work function of Ag(111) by deposition of sub-monolayer coverage of Rb. 1PP and 2PP spectroscopy of noble metal surfaces modified by alkali atom adsorption is well documented in literature [18-22], and specifically for alkali atoms on Ag(111) [23]. In Fig. S6, we show Rb-atom coverage dependent 1PP spectra excited with $\hbar\omega = 4.86$ eV photons from an Hg-lamp. The Rb coverage of <0.1 monolayer is increased to achieve work function reduction comparable to similar work of Barman et. al. (Fig. 5 in Ref. [22], $\hbar\omega \approx 5$ eV). For the clean Ag(111) surface, only the SS state is detected in 1PP due to its high work function [Fig. S6 (a) (left) and Fig. S6 (b)]. Gradually increasing Rb coverage decreases the work function and allows the resonant 1-photon SP transition to be detected [Fig. S6 (a) (right), excitation diagram in Fig. S6 (c)]. Most importantly, we observe a photoemission spectral element (“peak”) at $E_f \approx 3.7$ eV, $1\hbar\omega_p$, which shows a broad line shape both in energy as well as in momentum space. Based on the known band structure of Ag(111) [1,3,6,24], this spectral feature cannot be excited by single-particle excitations, because This energy falls into the band gap of Ag(111), and therefore there is no initial or final single-particle state that could be excited in 1PP to this energy. Instead, this feature is consistent with UV photons causing the excitation of the bulk plasmon of Ag, which decays to excite electrons from near $E_F$ to produce the $1\hbar\omega_p \approx 3.7$ eV feature. Moreover, this photoemission signal must involve a
decay of a collective excitation, because there are no single-particle initial or final states within the bulk band gap of Ag(111) at $k|| = 0$ that could be the origin of this emission (for details see main text). Also, the broad line shape is not compatible with single particle features in 1PP or 2PP spectra of Ag(111). We note that in the 1PP spectra of Ag thin films by Barman et al. a weak shoulder appears at $\sim 3.7$ eV, and thus may have the same origin [22]. We thus conclude that the decay of bulk plasmon quanta can preferentially excite electrons from $E_F$.

We note, that the Hg-lamp emission includes a line at $h\omega \approx 3.7$ eV (factor 15 weaker when compared to $h\omega \approx 4.86$ eV), which could lead to 1PP of SS state electrons to $E_F \approx 3.7$ eV. We exclude this as a possible contribution to the peak at $E_f \approx 3.7$ eV, however, because its line shape and $k||$-dispersion are significantly different from those of the SS state [cf. Fig. S6 (a)].

References.