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Phys. Rev. Lett. **123**, 017404 — Published 3 July 2019

DOI: 10.1103/PhysRevLett.123.017404

The nonlinear plasmonic photoelectron response of Ag(111)

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Photons can excite the 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 the electromagnetic energy and can drive nonlinear processes in electronic materials, particularly where their dielectric function $\varepsilon(\omega)$ approaches zero. We investigate the nonlinear angle-resolved two-photon photoemission (2PP) spectroscopy of Ag(111) surface through the $\varepsilon(\omega)$ near-zero region. In addition to the Einsteinian single-particle photoemission, the 2PP spectra report unequivocal signatures of nonlocal dielectric, plasmonically enhanced, excitation processes.

The complex dielectric tensor $\varepsilon(\omega)$ defines how electrons in a metal experience an optical field and participate in the nonlinear electro-optic response. The epsilon near zero (ENZ; Re[$\varepsilon(\omega)$]=0) condition defines the bulk plasmon frequency, ω_p, 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[$\varepsilon(\omega)$]<0), the screening in metals occurs mainly through a virtual plasmonic response, and is manifested by high reflectivity; for Re[$\varepsilon(\omega)$]$\cong$0, because for $\hbar\omega\cong\hbar\omega_p$, the screening by free electrons becomes ineffective [11,18-20,23,24]. Moreover, at ENZ, Im[$\varepsilon(\omega)$] rises stepwise [14], because for $\hbar\omega\cong\hbar\omega_p$ 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 $\hbar\omega_p$=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 $\hbar\omega$ 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 ≈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 $k_{||}$-momentum-resolved 2PP spectra for different $\hbar\omega$ and their profiles for normal emission ($k_{||}$ = 0 Å^{-1}); Figure 3 plots the photoelectron energies, E_f, relative to the Fermi energy, E_F, and intensities *vs*. $\hbar\omega$ for the spectral features.

The $E_f(k_{||})$ resolved 2PP spectra below (Fig. 1a,b) and above (Fig. 1c,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 $k_{||}$ ranges of SS and the SP transition are limited, respectively, by their dispersions to above E_F and the electron energy analyzer acceptance angle. Increasing $\hbar\omega$ to above $\hbar\omega_p$, however, causes the *bulk* SP transition to disappear, even though it can still be excited, but the *surface* SS and the n=1 image potential (IP) states remain and pass through resonance [Fig. 1(c), Fig. 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 $1\hbar\omega$, 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 ~50% with respect to

the SS photoemission [47]. Instead, we attribute its dramatic 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 coworkers [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 and Ref. [51]).

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$5 eV) [24,38,52]. Whether it also affects the 2PP from SS of Ag(111) is not clear, because our measurements cover a limited range ($\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 [Fig. 2(c), Fig. 3], its lineshape is asymmetric [see Fig. 1(c)-(d)], and it disperses over the accessible $k_{\|}$-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≈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. 1(a) and Ref. [32,47,53]}. Instead, Giesen *et al*. attributed the E_f≈ 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. The intensity of the $2\hbar\omega_p$ feature is inconsistent with a quadratic dependence on the n=1 IP state population for experiments with different pulse durations, when $\hbar\omega$ is varied, or in experiments where we deposit organic molecules [54] to quench the surface SS and n=1 IP state signals (supplemental material S2 and S3, Fig. S4). Instead, we attribute the $2\hbar\omega_p$-feature to decay of two bulk plasmon quanta, which can be excited for $\hbar\omega \cong \hbar\omega_p$ and must excite single photoelectrons from E_F to $E_f \approx 2\hbar\omega_p$. We note that 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≈7.9 eV [55]. Observation of the $2\hbar\omega_p$-feature on different crystalline planes of Ag can only be consistent with excitation of the bulk plasmon excitation, which is the only mode that could depend weakly on the crystal orientation. Also, in EELS spectral of Ag(111) with >70 eV electrons, a $2\hbar\omega_p$ loss peak has been reported at 7.6 eV [56,57], approximately where we detect the $2\hbar\omega_p$ decay.

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 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 ω_p that can act as a secondary excitation to excite additional *e-h* pairs. The decay of plasmons into single particle excitations is thought to excite electrons from E_F-ω_p up to E_F, to final states from E_F up to E_F+ω_p, with only the density-of-states determining the hot electron energy distribution [58]. 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 photoemission scenario is unconventional, but has precedent in *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) that the 2$\hbar\omega_p$-feature is strongly sensitive on temperature, implicating the electron occupation discontinuity at E_F. We note that that single-particle 2PP from E_F at $k_{||}$ = 0 Å^{-1} is not possible, because the band gap of Ag(111) extends from E-E_F=-0.4 to 3.9 eV [59]. The SS state just below E_F is also unlikely as the initial state, because (*i*) its $k_{||}$-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). In a many-body process, however, electrons from E_F can be photoemitted at $k_{||}$ = 0 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, ω_p decay excites electrons to E_f≈1$\hbar\omega_p$, as has been reported for Na/Ag(100) films [32], we lower the work function of Ag(111) by sub-monolayer chemisorption of Rb, which only modifies the surface electronic structure of Ag [60].

Indeed, 1PP spectra of Rb/Ag(111) with Hg-lamp excitation ($\hbar\omega \approx$ 4.86 eV; supplemental material S5, Fig. S6) 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 [39,55] 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←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 $\mathrm{Re}[\varepsilon(\omega)]<0$ through the multipole plasmon resonance. Pfeiffer and coworkers have described a similar scenario for intensification of 2PP by excitation of plasmonic fields in metal nanoparticles [61], 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 $\hbar\omega \cong \hbar\omega_p$, 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 [62] of plasmonic nanostructures up to fifth order of the plasmon field when exciting Au at moderate powers with an ultrafast Ti:sapphire laser oscillator [63]. 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 [3,26,27].

Acknowledgements

We are indebted to Thomas Fauster and Karsten Horn for discerning discussions, and financial support from DOE-BES Division of Chemical Sciences, Geosciences, and Biosciences Grant No. DE-SC0002313. M. R. acknowledges support through the Feodor Lynen Fellowship Program from the Alexander von Humboldt Foundation.

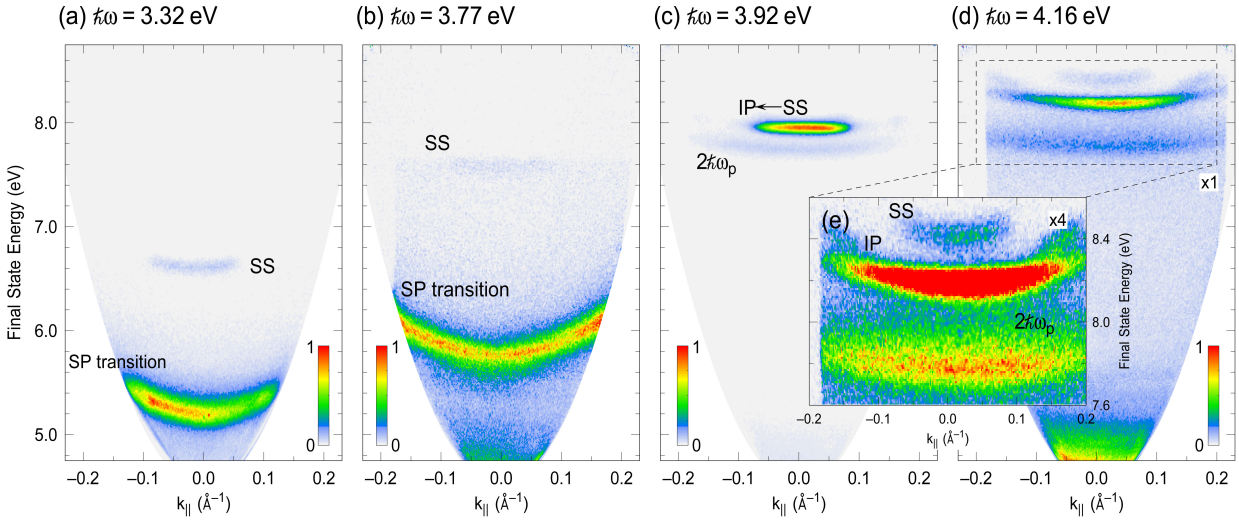

Figure 1| Energy and $k_{||}$-momentum resolved 2PP spectra for increasing excitation energies $\hbar\omega$. Each intensity color table is scaled separately; the spectral features are labelled in each spectrum. (a)/(b) For $\hbar\omega<\hbar\omega_p$, the SP transition intensity dominates that of the SS state. (c)/(d) For $\hbar\omega\geq\hbar\omega_p$, the SS and the n=1 IP states dominate the spectra, but the SP transition vanishes. An additional feature, which cannot be assigned to the single-particle band structure of Ag(111), appears at $E_f = 2\hbar\omega_p \approx 7.75$ eV. (e) Expanded and enhanced $E_f(k_{||})$-spectra from within the dashed box in (d) showing the $2\hbar\omega_p$-feature, as well as the n=1 IP and SS states (the color-scale is expanded four times).

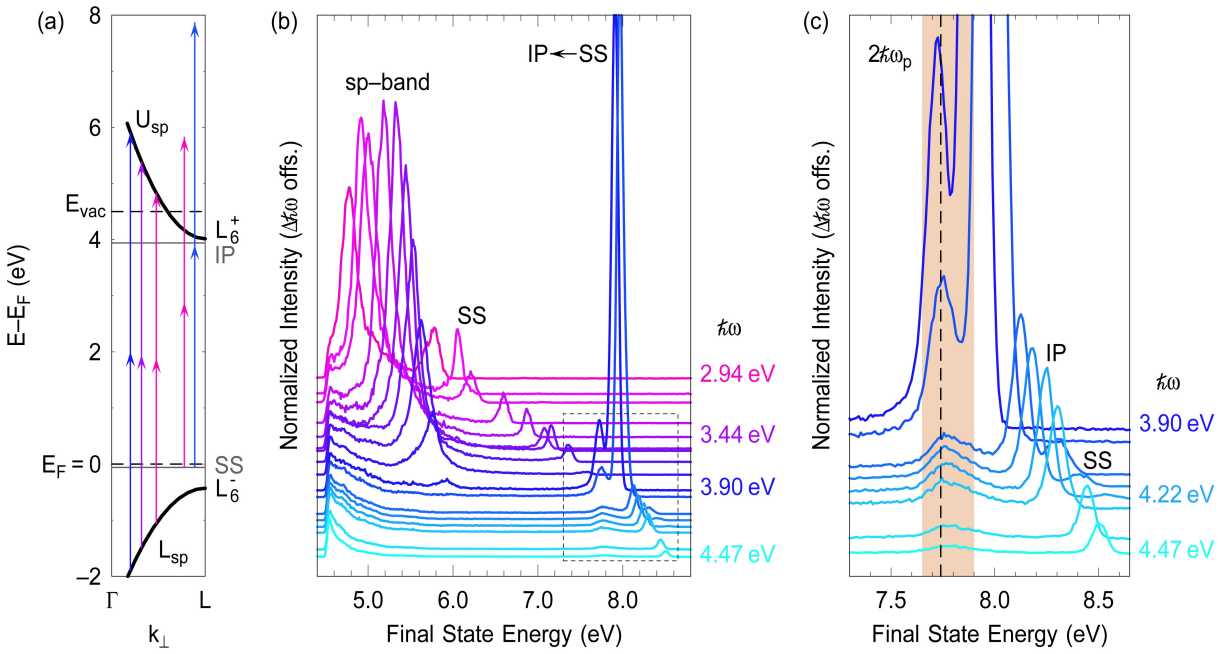

Figure 2| 2PP spectra and photoexcitation pathways in the 2.9 to 4.5 eV energy range for Ag(111) surface. (a) The single-particle band structure of Ag along the Γ-L ($k_\perp$) direction; the indicated optical transitions connect the free-electron like, L_{sp}, and the upper, U_{sp}, *sp*-bands as well as surface states (SS, IP). (b) 2PP spectra obtained by tuning $\hbar\omega$ through the ENZ range. The spectral $k_{||} = 0$ 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 labelled 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).

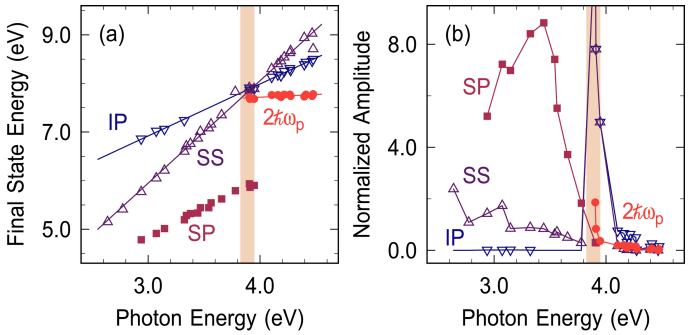

Figure 3| Quantitative evaluation of 2PP spectra of Ag(111) from Fig. 2 for $2.6<\hbar\omega<4.5$ eV ($k_{||}=0$ Å^{-1}); the brown shading highlights the *ENZ* region. (a) E_f vs. $\hbar\omega$ for the major spectroscopic features. Slopes of 1 (IP) and 2 (SS), indicate that electrons from these states are photoemitted by absorbing one- or two-photons. The $2\hbar\omega_p$-feature is only observed for $\hbar\omega\geq3.9$ eV and its E_f does not shift with $\hbar\omega$. The slope of the SP transition is defined by the two-photon resonance [42]. (b) Peak amplitudes *vs*. $\hbar\omega$: the SP transition amplitude peaks at $\hbar\omega\approx3.4$-3.5 eV, precipitously decreases towards $\hbar\omega\approx3.9$ eV, and vanishes above it. The $2\hbar\omega_p$-feature appears above $\hbar\omega\approx3.9$ eV. The resonant $n=1$ IP ← SS excitation at $\hbar\omega=3.92$ eV strongly modulates intensities of the coupled states.

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