Photoemission footprints of extrinsic plasmarons

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A prediction of how to experimentally distinguish excitations of extrinsic plasmarons from intrinsic plasmarons is presented. In surface systems where excitations of acoustic surface plasmons are possible, it is shown that the photoelectron yield in normal photoemission should decay according to an inverse square-root dependence with respect to the photon energy. A computational analysis of the system $p(2\times2)$-K/graphite confirms this prediction.

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I. INTRODUCTION

In photoemission experiments, photoelectrons carry information of many-body interactions created by the photohole and by the escaping photoelectron itself. In the case of strong coupling between the photohole or induced density caused by the photoelectron, and plasmon excitations, the quasiparticle picture breaks down and new loss peaks appear in the photoemission spectrum. The excitation formed by the photohole-plasmon interaction defines the *intrinsic* plasmaron and the photoelectron-plasmon interaction defines the *extrinsic* plasmaron [1,2].

For systems with a surface-state band crossing the Fermi level, a plasmon localized at the surface and characterized by a sound-like dispersion, the so-called acoustic surface plasmon (ASP), has been predicted to exist [3,4]. Later on, electron energy loss spectroscopy (EELS) experiments have confirmed the presence of the ASP mode at the Be(0001) [5,6] and noble metal surfaces [7–14], in good agreement with calculations, and also for graphene adsorbed on metal substrates [15–22]. In cases when surface localized quantum well states are formed, e.g., when atomic layers of alkali metals are adsorbed on a metal surface the possibility opens up to design ASP by varying the depth of the quantum well (type of alkali atoms) and the width of the quantum well (number of layers).

A challenge is to find out about the relative occurrence of the *intrinsic* and *extrinsic* plasmarons from a photoemission experiment. In this paper we show that, for a surface system with ASP, the *extrinsic* plasmaron excitation channel can be traced by looking at the photon energy dependence of the photoelectron yield in the direction normal to the surface plane. Simple kinematics indicate an inverse square-root dependence, while the *intrinsic* plasmaron is not expected to depend on the photon energy.

Here we present results from an extension of a previous calculation on the system: a monolayer potassium adsorbed on graphite [$p(2\times2)$-K/graphite] [23].

II. THEORY

The energy loss induced by the escaping photoelectron in an angle-resolved photoemission spectroscopy (ARPES) experiment is given by the rate of electronic surface excitations. Applying linear response theory the rate of *extrinsic* plasmaron excitation is given by [23]

$$W(\omega,\tilde{z}) = \frac{4\pi}{A}\sum_{\mathbf{q}_\parallel}\frac{e^{-q_\parallel\tilde{z}}}{q_\parallel}\,\mathrm{Im}[g(\mathbf{q}_\parallel,\omega)], \tag{1}$$

where A is the area of the surface, g the surface response function [24], $\mathbf{q}_\parallel$ the two-dimensional (2D) in-plane momentum, $q_\parallel = |\mathbf{q}_\parallel|$, and $\tilde{z}$ the distance between the escaping photoelectron and the surface. We consider at this point a general system with an ultrathin metal adlayer adsorbed on metal surface. We assume formation of a surface quantum well (QW) hosting a QW-state band and as a result the existence of ASP.

A photoexcited electron with an initial parallel wave vector $\mathbf{k}'_\parallel$ will with some probability be inelastically scattered to $\mathbf{k}_\parallel$ while exciting an ASP with momentum $\mathbf{q}_\parallel = \mathbf{k}_\parallel - \mathbf{k}'_\parallel$. The photoelectrons with momentum $\mathbf{k}_\parallel = \mathbf{k}'_\parallel$ will yield the main peak, corresponding to the electrons having absorbed fully the photon energy. The width of this elastic peak reflects the finite lifetime of the photohole left behind. In addition a satellite structure might appear at higher binding energies due to scattering from all $\mathbf{k}'_\parallel$ and $\mathbf{k}_\parallel$, satisfying $\mathbf{k}_\parallel = \mathbf{k}'_\parallel + \mathbf{q}_\parallel$, having excited an ASP with momentum $\mathbf{q}_\parallel$. If this satellite structure gives rise to a distinct peak an *extrinsic* plasmaron excitation is realized.

We calculate the $\mathbf{k}_\parallel$-resolved photoelectron energy loss per time unit due to the ASP excitations, which is equivalent to the dispersion of the *extrinsic* plasmaron excitations. This can be carried out from the expression given in Eq. (1),

$$W(k_\parallel,\epsilon,\tilde{z}) = \frac{2}{\pi}\int_0^{k_F} dk'_\parallel \int_0^{2\pi} d\alpha\,\frac{k'_\parallel}{q_\parallel}\,e^{-q_\parallel\tilde{z}}\Theta(q_{\max}-q_\parallel) \times\mathrm{Im}[g(q_\parallel,\epsilon-\epsilon_b+\hbar\omega(k'_\parallel))], \tag{2}$$

where k_F is the band Fermi wave vector, $k_\parallel = |\mathbf{k}_\parallel|$, $k'_\parallel = |\mathbf{k}'_\parallel|$, and α is the angle between the vectors $\mathbf{k}_\parallel$ and $\mathbf{k}'_\parallel$. $\Theta(x)$ is the Heaviside step function, ϵ_b is the binding energy, $q_\parallel = (k_\parallel^2 + k_\parallel'^2 - 2k_\parallel k'_\parallel\cos\alpha)^{1/2}$, $q_{\max}$ is the maximum wave vector up to which the ASP dispersion is well defined, and $\hbar\omega(k_\parallel)$-ϵ_b is the band dispersion relative to the Fermi energy.

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The ARPES intensity is given by integrating in time the excitation rate W

$$I(k_\parallel,\epsilon;h\nu) = \int_0^\infty W(k_\parallel,\epsilon,\tilde{z}(t))dt, \tag{3}$$

but as $d\tilde{z} = k_\perp dt$, where $k_\perp$ is the perpendicular momentum of the escaping photoelectron, we can now integrate with respect to $\tilde{z}$, obtaining the photon energy dependence of the *extrinsic* plasmaron dispersion. Simple kinematics in terms of photon energy $h\nu$, work function ϕ, and QW binding energy ϵ_b yields

$$k_\perp^2 = 2(h\nu - \phi - \epsilon_b - \epsilon + \hbar\omega(k'_\parallel)) - k_\parallel^2. \tag{4}$$

We then have the photon energy dependent intensity of *extrinsic* plasmaron excitations:

$$I(k_\parallel,\epsilon;h\nu) = \frac{2}{\pi}\int_0^{k_F} dk'_\parallel \int_0^{2\pi} d\alpha \frac{k'_\parallel}{k_\perp q_\parallel^2}\Theta(q_{\max} - q_\parallel) \times \mathrm{Im}[g(q_\parallel,\epsilon - \epsilon_b + \hbar\omega(k'_\parallel))]. \tag{5}$$

The expression in Eq. (5) forms the footprint of *extrinsic* plasmaron excitations. In the case of normal photoemission ($\mathbf{k}_\parallel = 0$), when the photon energy $h\nu$ exceeds $\phi + \epsilon_b$, the intensity of the *extrinsic* plasmaron excitations will decrease with photon energy accordingly: $I \sim 1/\sqrt{h\nu}$. This result can be traced back to the exponential decay of the external potential (generated by the escaping photoelectron) with respect to $\tilde{z}$. In the next section we illustrate this for a specific system.

III. CALCULATIONS

With this theoretical background we proceed to a specific system: a monolayer of potassium on graphite, $p(2\times2)$-K/graphite. According to first-principles calculations by Chis *et al.* [25], a quasi-2D QW system is formed by the potassium overlayer with an energy band centered at the $\bar{\Gamma}$ point of the Brillouin zone (BZ) (see the red colored line in Fig. 1). Another quasi-2D system is formed in the carbon atomic layer below the QW system, marked by blue color.

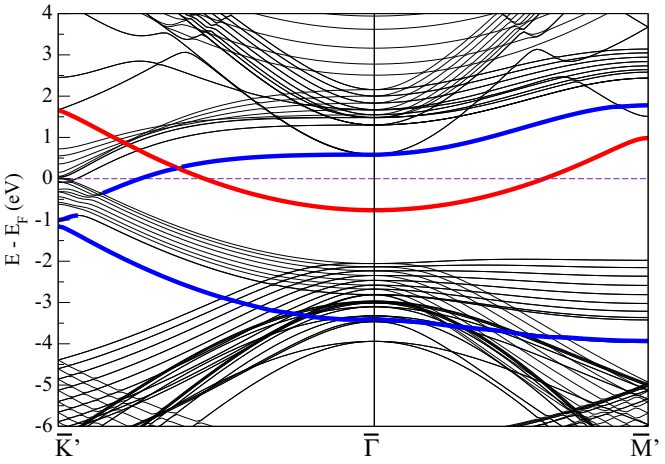

FIG. 1. (Color online) Calculated $p(2\times2)$-K/graphite band structure [25]. Red and blue color lines indicate the quantum well band and the lowest and the highest branches of the folded π^* and π bands, respectively. $\bar{K}'$ and $\bar{M}'$, represent the $\bar{K}$ and $\bar{M}$ points of the folded band structure due to the (2×2) overlayer of potassium.

Due to the larger Fermi surface of the QW band compared to the Fermi surface of the graphene-like uppermost graphite layer, low-energy excitations in the QW band will dominate. Moreover, the highest Fermi velocity in the graphene-like system is essentially the same as in the bulk carbon system. As a result a separate plasmonic mode corresponding to an out-of-phase charge oscillation in these two carbon systems cannot be realized. Thus our analysis is focused on the plasmon related to the QW band. It should be noted however, that in the calculation of the surface response function $g(\mathbf{q}_\parallel,\omega)$ we include quantum states from all the systems.

A. Acoustic surface plasmons

We have previously calculated [23] the surface loss function, $\mathrm{Im}[g(\mathbf{q}_\parallel,\omega)]$, within the time-dependent density functional theory scheme [26]. The surface loss function versus ω and $\mathbf{q}_\parallel$ reveals a linear sound-like dispersion $\omega(\mathbf{q}_\parallel)$ indicating the existence of ASP as a well-defined collective excitation in the energy range 0–0.6 eV with a momentum transfer span up to about 0.1 a.u. The extracted dispersion is shown Fig. 2. At larger momentum transfers, where the ASP dispersion is depicted by the dashed lines, this mode becomes strongly damped. Beyond this region for $q_\parallel \gtrsim 0.13$ a.u. it ceases to exist since the coherence of single electron excitations forming the collective plasmon excitation is lost due to incoherent electron-hole pair excitations. In Fig. 2 one can notice that the ASP dispersions along the $\bar{\Gamma}$-$\bar{M}$ and $\bar{\Gamma}$-$\bar{K}$ directions are very similar. Based on this observation we will further on assume that the ASP dispersion is isotropic in the surface plane.

The average slope of the ASP dispersion yields a group velocity of $c \approx 0.22$ a.u. which, according to Pitarke *et al.* [27], is set by the Fermi velocity of the 2D carriers in the QW band. This is consistent with the band structure in Fig. 1 where the slope of the QW band when crossing the Fermi level is similar: $v_F \approx 0.23$ a.u. [23].

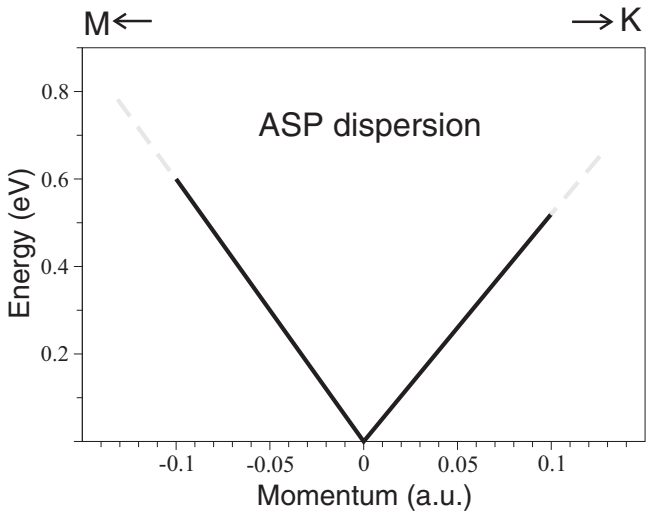

FIG. 2. ASP dispersion of the system $p(2\times2)$-K/graphite. The arrows indicate the directions $\bar{\Gamma}$-$\bar{M}$ and $\bar{\Gamma}$-$\bar{K}$. The solid lines are extracted from the calculated $\mathrm{Im}[g(\mathbf{q}_\parallel,\omega)]$ in [23]. The dashed lines indicate the strong damping of the ASP due to incoherent excitations of electron-hole pairs.

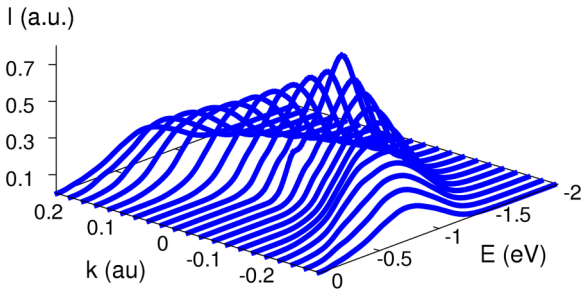

FIG. 3. (Color online) Photoelectron intensity as a function of $k_\parallel$ and $E = -\epsilon_b - \epsilon$, where ϵ is the plasmaron excitation energy. The photon energy is 10 eV.

B. Plasmaron excitations

For the system $p(2\times2)$-K/graphite, we have $k_F = 0.23$ a.u., $q_{\max} = 0.1$ a.u., $\epsilon_b = 0.76$ eV, and the QW band dispersion is approximately parabolic: $\hbar\omega(k_\parallel) = \epsilon_b(k_\parallel/k_F)^2$. The calculated ARPES intensity according to Eq. (2) gives the *extrinsic* plasmaron excitations and is shown as function of parallel momentum and energy in Fig. 3. The peak at $k_\parallel = 0$ appears at about 1.29 eV below the Fermi level which is 0.53 eV below the bottom of the QW band ($-\epsilon_b$). It is seen in Fig. 3 that the energy position of the QW band gives rise to a small kink.

Calculating the photon energy dependent photoelectron yield according to Eq. (5), we reveal the footprint of *extrinsic* plasmaron excitations. The work function of $p(2\times2)$-K/graphite is taken as $\phi = 2.3$ eV [28,29]. In Fig. 4 we show the photon energy dependence of the photoelectron intensity for normal emission ($k_\parallel = 0$).

We then fit the maximum intensity in normal emission versus photon energy $h\nu$ to a functional form given by

$$I_{\max}(h\nu) = A(h\nu)^{-\alpha}. \tag{6}$$

With this fitting procedure, illustrated in Fig. 5, we obtain $A = 1.99$ a.u. and $\alpha = 0.49$. In order to have positive kinetic energy we require a minimum photon energy given by $h\nu_{\min} = \phi + \epsilon_b + \epsilon \approx 3.6$ eV. Thus we confirm the expected inverse square-root dependence of the photoelectron intensity with respect to the photon energy as discussed previously.

IV. SUMMARY AND CONCLUSIONS

In the photoemission experiment, the predicted footprint of the *extrinsic* plasmarons, generated by the escaping photoelectron, is the inverse square-root dependence of the photon energy. This enables a possibility to distinguish *extrinsic* from *intrinsic* plasmarons, where the latter is generated by the photohole. Following up a previous theoretical study of the system $p(2\times2)$-K/graphite [23] shows that this prediction seems reliable.

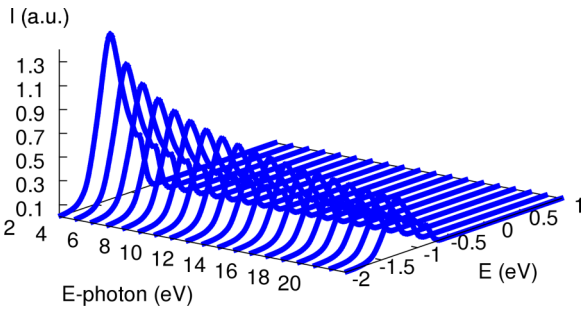

FIG. 4. (Color online) Photoelectron intensity in the $\bar{\Gamma}$ point ($k_\parallel = 0$) as a function of photon energy and $E = -\epsilon_b - \epsilon$, where ϵ is the plasmaron excitation energy.

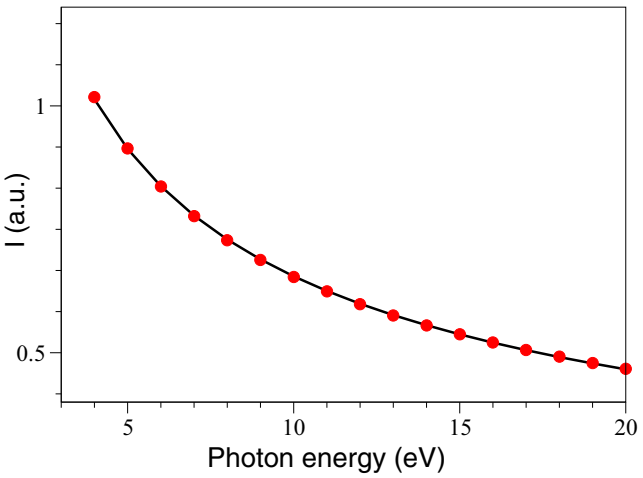

FIG. 5. (Color online) Solid line: Calculated photoelectron yield versus photon energy at the plasmaron peak for normal emission ($k_\parallel = 0$). The peak is located 1.29 eV below the Fermi energy. Filled circles: Fitted intensity versus photon energy $h\nu$ with to functional form given in Eq. (6) with $A = 1.99$ and $\alpha = 0.49$.

In general, for a surface system in which excitations of acoustic surface plasmons (ASP) is possible, the *extrinsic* type of plasmarons are likely to be excited in photoemission. However, the relative importance of *intrinsic* and *extrinsic* plasmarons is an open question. EELS measurements could give important additional information, as it will give a hint about the existence of *extrinsic* plasmarons, the reason being that in EELS the electrons scattering off the surface will suffer a characteristic energy loss if excitations of ASP take place and in addition if the probe-electron plasmon interaction is strong enough.

An interesting system to investigate further is graphene adsorbed on metal surfaces. In this case excitations of ASP is possible [15–22]. Utilizing our proposed expected photon energy dependence of excitations of *extrinsic* plasmarons it might be possible to judge the relative importance of *extrinsic* and *intrinsic* plasmaron excitations.

Referring to the aim of photonics, converting long-wavelength light to short-wavelength surface plasmons, the presence of *extrinsic* plasmarons could be of importance. The possibility to control, by means of changing the photon energy, the yield of surface plasmon excitations driven by the photoelectrons (*extrinsic* plasmaron excitations) opens a possibility to control the conversion yield of photons to surface plasmons.

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