

Plasmaron excitations in p(2 × 2)-K/graphiteV. Chis,^{1,*} V. M. Silkin,^{1,2,3} and B. Hellsing^{1,4}¹*Donostia International Physics Center (DIPC), 20018 San Sebastián, Spain*²*Depto. de Física de Materiales, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain*³*IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain*⁴*Department of Physics, Gothenburg University, S-41296 Gothenburg, Sweden*

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Plasmarons formed by the compound of photoelectrons and acoustic surface-plasmon excitations is investigated in the system p(2 × 2)-K/graphite. The physics behind this type of plasmarons (*e* plasmarons) differs from the physics of plasmarons recently found in graphene, where the loss feature is argued to result from the photohole-plasmon interaction (*h* plasmarons). Based on *first principles* methods we calculate the dispersion of the *e*-plasmaron excitation rate, which yields a broad feature below the parabolic quantum-well band with a peak about 0.4 eV below the quantum-well band at the $\bar{\Gamma}$ point.

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I. INTRODUCTION

In photonics, light is used for information processing. The dimension of channels directing the light is limited by its wavelength, which is typically several hundred nanometers. However, if the information could be transferred to plasmons, these could in turn be guided through structures measured on the nanometer scale, because the plasmon wavelength is of the order nanometers. This is the basis of the plasmonic devices that merge photonics and electronics [1–4]. The transformation of information from a photon to a plasmon requires some intermediate electronic excitation because the photon carries negligible momentum. These intermediate excitations could be elementary charge excitations, electrons or holes.

Angle-resolved photoemission spectroscopy (ARPES) is a suitable tool to obtain information about the efficiency of the link between the incoming photon and the excitation of plasmons. However, the outgoing photoelectron carries information not only about the *photohole-plasmon* interaction described by the spectral function, but also about the direct *photoelectron-plasmon* interaction. We report on the importance of the photoelectron-acoustic surface plasmon interaction, yielding what we denote *e* plasmarons.

ARPES is of tremendous importance for understanding the properties of solids, not only as a tool to map the single-electron band structure of compounds, but also to learn about the influence of various many-body effects such as the electron-electron interaction of itinerant electrons [5–8], local electron-electron Coulomb repulsion in strongly correlated materials [9], the electron-phonon interaction [10,11], and electron-plasmon interaction exciting so-called plasmarons [5,12]. All these many-body effects renormalize the band structure observed in ARPES.

The photoemission process can be divided into three steps: optical excitation, propagation of the photoelectron to the surface, and finally its escape into the vacuum. In the first step the spectral function $A(\mathbf{k}, \omega)$, describing the photohole relaxation, is in general considered to produce the bulk part of the

photoemission spectrum. This *sudden approximation* is not appropriate in many cases. The second step is known to yield surface effects leading to misinterpretations of bulk properties [13–15].

The features appearing in the photoemission spectra at binding energies higher than the single-particle bands could reflect *extrinsic* loss processes taking place in steps two and three. However, this part of the spectrum could also reflect *intrinsic* processes, which should be taken care of by the spectral function, giving rise to, e.g., lower-Hubbard bands for strongly correlated materials. As pointed out by Guzzo *et al.* [16], the analysis and understanding of this part of the spectrum is poor in valence-band spectroscopy.

A recent study of graphene, comparing ARPES data with calculations of the spectral function and focusing on the dynamics of the electron-electron interaction, suggests the presence of plasmarons [17]. The plasmaron, a composite excitation due to the long-range interaction between elementary charges (electrons or holes) and plasmons, was suggested almost half a century ago [12,18]. The interpretation of ARPES data [17] is that the photoelectrons reaching the detector carry information about the interaction between the hole left behind and plasmons. We denote these excitations *h* plasmarons, where *h* refers to the hole-plasmon interaction. In a recent tunneling spectroscopy study, plasmaron excitations of the hole type is claimed to be observed also for two-dimensional (2D) quantum-well systems by Dial *et al.* [19]. A recent theoretical study of bilayer graphene, calculating the spectral function and taking into account the electron-electron interaction within the random-phase approximation, reveals plasmaron excitations [20]. The excitations in this case are due to the photohole-plasmon interaction and are thus *h* plasmarons. These observations together indicate that plasmarons are a general feature of quasi-2D electron systems.

There is a possibility that, in step three of the photoemission process, the unscreened photoelectron, when detached from the electron gas of the compound on its way to the spectrometer, but still close enough to induce excitations in the material, will create collective excitations and thus lose some of its energy and momentum. This phenomena should, in particular, be important in cases when low-energy

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surface-localized plasmons could be excited. Thus it is in principle possible that the additional lower-energy feature in the ARPES spectrum is due to plasmon excitations in the solid due to the electromagnetic field created by the decoupled outgoing photoelectron. In this case the elementary particle is an electron and not a hole, and we denote the composite “particle” an e plasmaron. The picture is obviously different from the interpretation that the feature reflects h plasmaron excitations in the solid.

In the present study we focus on the third step of the photoemission process for the system $p(2 \times 2)$ -K/graphite and calculate the dispersion of the e -plasmaron excitation rate. The system is ideal for the study of the third step due to the quasi-2D character of the electron structure, which rules out the importance of the second step. The results indicate that losses due to the interaction of the escaping photoelectron and surface localized plasmons could give rise to satellites in the ARPES spectrum. The ARPES data of Algdal *et al.* [21] for the system $p(2 \times 2)$ -K/graphite show an asymmetry of the quantum-well peak near normal emission which is consistent with additional losses below the peak.

For systems with an electron surface-state band crossing the Fermi level, a plasmon localized at the surface and characterized by a sound-like dispersion (so-called acoustic surface plasmons or ASPs) has been predicted to exist [22–25]. Later on, electron-energy-loss spectroscopy experiments confirmed the presence of the ASP mode at the Be(0001) surface, in good agreement with *first principles* calculations [26], noble-metal surfaces [27–31], and graphene adsorbed on metal substrates [32–34]. 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 ASPs by varying the depth (type of alkali-metal atoms) and the width (number of layers) of the quantum well.

II. THEORY

The energy loss induced by the escaping photoelectrons in an ARPES experiment is given by the rate of electronic surface excitations. In first-order time-dependent perturbation theory, (i.e., the “golden rule”) we have that the rate of e -plasmaron excitation is given by [35]

$$W(\omega) = 2\pi \sum_{\mathbf{k}_\parallel, \mathbf{k}'_\parallel, n, n'} (f_{n\mathbf{k}_\parallel} - f_{n'\mathbf{k}'_\parallel}) |\langle \psi_{n'\mathbf{k}'_\parallel}^* | \phi_{\text{scf}} | \psi_{n\mathbf{k}_\parallel} \rangle|^2 \times \delta(\epsilon_{n'\mathbf{k}'_\parallel} - \epsilon_{n\mathbf{k}_\parallel} - \hbar\omega), \quad (1)$$

where f is the Fermi-Dirac factors, $\psi_{n\mathbf{k}_\parallel}$ the one-electron wave functions with the corresponding energies $\epsilon_{n\mathbf{k}_\parallel}$, and ϕ_{scf} is the self-consistent potential caused by the photoelectron which drives the single-electron excitations from state $n\mathbf{k}_\parallel$ to state $n'\mathbf{k}'_\parallel$. Equation (1) can be expressed in terms of the bare density-density response function $\chi_0(\mathbf{r}, \mathbf{r}', \omega)$ evaluated in a slab geometry [36]:

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\mathbf{k}_\parallel, \mathbf{k}'_\parallel, n, n'} (f_{n\mathbf{k}_\parallel} - f_{n'\mathbf{k}'_\parallel}) \frac{\psi_{n\mathbf{k}_\parallel}^*(\mathbf{r}) \psi_{n'\mathbf{k}'_\parallel}(\mathbf{r}) \psi_{n'\mathbf{k}'_\parallel}^*(\mathbf{r}') \psi_{n\mathbf{k}_\parallel}(\mathbf{r}')}{\epsilon_{n'\mathbf{k}'_\parallel} - \epsilon_{n\mathbf{k}_\parallel} - \hbar\omega + i\delta}. \quad (2)$$

Then we have

$$W(\omega) = -2\text{Im} \left[\int d\mathbf{r} \int d\mathbf{r}_1 \chi_0(\mathbf{r}, \mathbf{r}_1, \omega) \phi_{\text{scf}}(\mathbf{r}, \omega) \phi_{\text{scf}}^*(\mathbf{r}_1, \omega) \right],$$

where Im represents the imaginary part. Note that we use the notation $\mathbf{r} \equiv (\mathbf{r}_\parallel, z)$ and $\mathbf{k} \equiv (\mathbf{k}_\parallel, k_z)$ for vectors in real and reciprocal spaces, respectively. Within a linear-response theory we have in momentum and frequency space

$$\begin{aligned} \chi_0 \phi_{\text{scf}} &= \chi_0 \phi_{\text{ext}} + \chi_0 \delta\phi \\ &= \chi_0 \phi_{\text{ext}} + \chi_0 K \delta n \\ &= (\chi_0 + \chi_0 K \chi) \phi_{\text{ext}} \\ &= \chi \phi_{\text{ext}} = \delta n, \end{aligned} \quad (3)$$

where ϕ_{ext} is the external potential due to the photoelectron, and $\delta\phi$ is the induced potential caused by the induced electron density δn . The kernel K in real space is explicitly given by

$$K(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + V'_{xc}[n_0(\mathbf{r})] \delta(\mathbf{r} - \mathbf{r}'), \quad (4)$$

where V_{xc} is the exchange-correlation potential. According to Eq. (3), the full response function is determined self-consistently by the Dyson equation

$$\chi = \chi_0 + \chi_0 K \chi. \quad (5)$$

The induced density δn is given by

$$\begin{aligned} \delta n(\mathbf{r}, \omega) &= \int d\mathbf{r}_1 \chi(\mathbf{r}, \mathbf{r}_1, \omega) \phi_{\text{ext}}(\mathbf{r}_1, \omega) \\ &= \int d\mathbf{r}_1 \chi_0(\mathbf{r}, \mathbf{r}_1, \omega) \phi_{\text{scf}}(\mathbf{r}_1, \omega). \end{aligned} \quad (6)$$

We can thus write

$$\begin{aligned} W(\omega) &= -2 \text{Im} \left[\int d\mathbf{r} \phi_{\text{scf}}^*(\mathbf{r}, \omega) \delta n(\mathbf{r}, \omega) \right] \\ &= -2 \text{Im} \left[\int d\mathbf{r} \phi_{\text{ext}}^*(\mathbf{r}, \omega) \delta n(\mathbf{r}, \omega) \right] \\ &\quad - 2 \text{Im} \left[\int d\mathbf{r} \int d\mathbf{r}' K^*(\mathbf{r}, \mathbf{r}') \delta n^*(\mathbf{r}', \omega) \delta n(\mathbf{r}, \omega) \right] \end{aligned} \quad (7)$$

Now, $K(\mathbf{r}, \mathbf{r}')$ is real and symmetric with respect to interchanging the variables \mathbf{r} and \mathbf{r}' and thus the second term will vanish and we have

$$W(\omega) = -2 \text{Im} \left[\int d\mathbf{r} \phi_{\text{ext}}^*(\mathbf{r}, \omega) \delta n(\mathbf{r}, \omega) \right]. \quad (8)$$

We consider an ARPES experiment and the possibility that an ejected photoelectron will lose part of its energy somewhere in between the surface and the detector at an average distance z_0 from the surface. We keep z_0 as a parameter to vary later on. We assume that the distance from the surface is far enough that the “spill-out” electron density from the surface is negligible at $z = z_0$. The external potential must then fulfill the Laplace equation [35]

$$\phi_{\text{ext}}(\mathbf{r}_\parallel, z, \omega) = -\frac{1}{A} \sum_{\mathbf{q}_\parallel} \frac{2\pi}{q_\parallel} e^{q_\parallel(z-z_0)} e^{i(\mathbf{q}_\parallel \cdot \mathbf{r}_\parallel - \omega t)}, \quad (9)$$

where A is the surface area and $q_\parallel = |\mathbf{q}_\parallel|$. The rate of energy loss can then be expressed in terms of the surface response

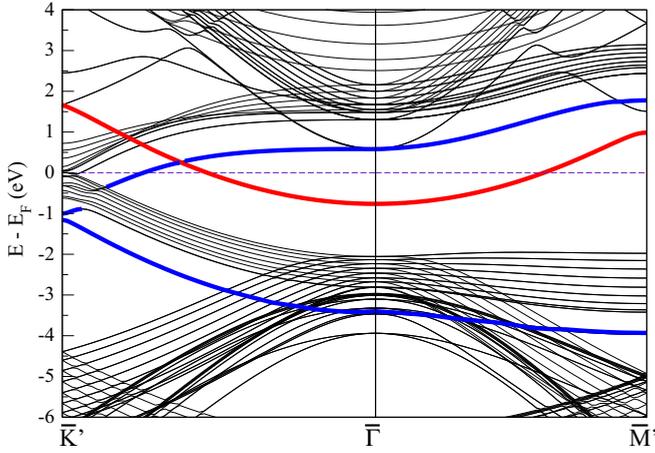


FIG. 1. (Color online) Calculated p(2 × 2)-K/graphite band structure [38]. Red and blue lines indicate the quantum-well band and the lowest and highest branches of the folded π^* and π bands, respectively. \bar{K}' and \bar{M}' represent the \bar{K} and \bar{M} points, respectively, of the folded band structure due to the (2 × 2) overlayer of potassium.

function $g(\mathbf{q}_{\parallel}, \omega)$ [37]:

$$g(\mathbf{q}_{\parallel}, \omega) = \int dz e^{q_{\parallel}z} \delta n(z, \mathbf{q}_{\parallel}, \omega) \quad (10)$$

and accordingly

$$W(\omega) = \frac{4\pi}{A} \sum_{\mathbf{q}_{\parallel}} \frac{e^{-q_{\parallel}z_0}}{q_{\parallel}} \text{Im}[g(\mathbf{q}_{\parallel}, \omega)]. \quad (11)$$

III. CALCULATIONS

With this theoretical background we proceed to the specific system, a monolayer of potassium on graphite, p(2 × 2)-K/graphite. According to the *first principles* calculations by Chis *et al.* [38] two quasi-2D electron systems on top of each other are formed. At the top, a quantum-well (QW) 2D system is formed with an energy band centered at the $\bar{\Gamma}$ point of the Brillouin zone (BZ) (see red-colored line in Fig. 1). Another quasi-2D system is formed below the QW system and is essentially located at the uppermost single graphite layer. The band structure localized to this doped graphene type of layer has an antibonding and a bonding character. The lower branch of the downshifted antibonding π^* band [folded due to the (2 × 2) potassium overlayer] and the upper branch of the folded bonding π band are marked blue in Fig. 1. The bands meet at the \bar{K}' point of the BZ, about 1 eV below the Fermi level.

A. Acoustic surface plasmons

We proceed and calculate the linear response spectrum caused by the escaping photoelectron, still close to the surface but detached from the surface electron density. In order to find out about the existence of ASPs we calculated the surface loss function $\text{Im}[g]$ within the time dependent density functional theory scheme [39] with one-electron wave functions and corresponding eigenenergies from the band-structure calculation discussed above. The result of the calculation is shown in Fig. 2

Indeed we find the ASP in the energy range 0–0.7 eV with a momentum transfer span up to about 0.12 a.u. The

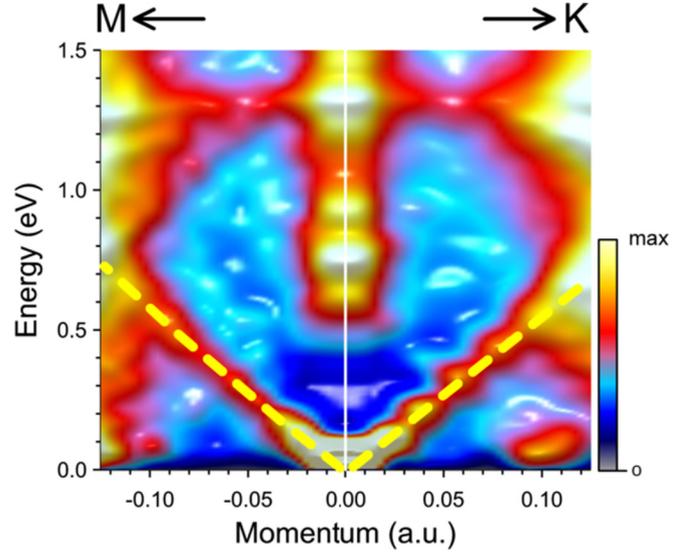


FIG. 2. (Color online) The calculated normalized surface loss function, $\text{Im}[g(\mathbf{q}_{\parallel}, \omega)/(q_{\parallel}\omega)]$, along the $\bar{\Gamma}$ - \bar{M} and $\bar{\Gamma}$ - \bar{K} directions. Dashed lines highlight the sound-like dispersion of the ASP. The features at higher energies correspond to interband transition not relevant for this work.

interpretation is that, for $q_{\parallel} > 0.12$ a.u., the coherence of single-electron excitations forming the collective plasmon excitation is lost due to incoherent electron-hole pair excitations. In Fig. 2 we notice that the ASP dispersion 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 (x, y) plane.

Having *two* 2D systems on top of each other could in principle lead to two branches in the ASP dispersion. However, there is clearly only one ASP branch with a group velocity of $c = 0.24$ a.u. at small q_{\parallel} and reducing down to 0.22 a.u. at higher q_{\parallel} . The initial velocity c should, according to Pitarke *et al.* [40], be set by the Fermi velocity of the 2D carriers. This is consistent with the band structure in Fig. 1. The slope of the bands when crossing the Fermi level, moving away from the $\bar{\Gamma}$ point for the QW system and away from the \bar{K} point for the “graphene” system happens to be very similar: $v_F \approx 0.23$ a.u.

B. e-plasmaron dispersion

A photoexcited electron with initial parallel wave vector \mathbf{k}'_{\parallel} will with some probability be inelastically scattered to \mathbf{k}_{\parallel} while exciting an ASP with momentum $\mathbf{q}_{\parallel} = \mathbf{k}_{\parallel} - \mathbf{k}'_{\parallel}$. Thus the yield of photoelectrons with momentum \mathbf{k}_{\parallel} will have a main peak, corresponding to the electrons with initial momentum \mathbf{k}_{\parallel} having absorbed fully the photon energy and with a broadening due to the finite lifetime of the photohole left behind. In addition a satellite structure will appear at higher binding energies due to scattering from all \mathbf{k}'_{\parallel} satisfying $\mathbf{k}'_{\parallel} = \mathbf{k}_{\parallel} - \mathbf{q}_{\parallel}$, having excited an ASP with momentum \mathbf{q}_{\parallel} .

In the energy range of the ASP, 0–0.5 eV, the electron group velocity scanned over the entire BZ indicates that the largest contribution to the imaginary part of the dielectric function comes from the QW band, which reflects the fact that the density of states of the quasi-2D electron gas of the QW is

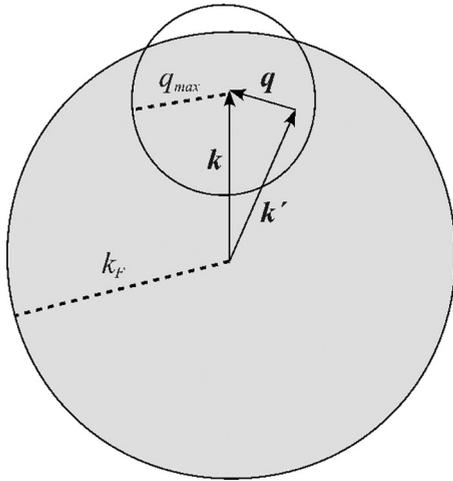


FIG. 3. Illustration of the integration performed in Eq. (12). The grey area represents the occupied part of the 2D electron states with the Fermi-momentum radius k_F . For any fixed vector $\mathbf{k} \equiv \mathbf{k}_{||}$ we integrate over all occupied states $\mathbf{k}' \equiv \mathbf{k}'_{||}$ enclosed in the circular disk with the radius given by the maximum absolute magnitude of the ASP wave vector q_{\max} .

fairly independent of energy, while for the graphene layer it decreases approximately linear when approaching the \bar{K} point. This means that, near the Fermi level, the electron density of states will be comparatively low in the graphene layer.

Based on this we will in this study only consider the e -plasmon excitations due to the coupling between the photoelectron, originating from the QW band with the ASP. We calculate the $\mathbf{k}_{||}$ -resolved photoelectron energy loss due to ASP excitations, which is equivalent to the dispersion of the e -plasmon excitations. This can be carried out from the expression given in Eq. (11). The QW band structure shown in Fig. 1 reveals that the dispersion along the $\bar{\Gamma}$ - \bar{M}' and $\bar{\Gamma}$ - \bar{K}' directions are similar. Thus we will assume that the QW band is isotropic in the surface plane, just as we previously concluded considering the ASP dispersion.

For a fixed vector $\mathbf{k}_{||}$ we integrate over all occupied states $\mathbf{k}'_{||}$ (gray area in Fig. 3) enclosed in the circular disk with a radius given by q_{\max} (illustrated in Fig. 3):

$$W(k_{||}, \epsilon) = \frac{2}{\pi} \int_0^{k_F} dk'_{||} \int_0^{2\pi} d\alpha \frac{k'_{||}}{q_{||}} e^{-q_{||}z_0} \Theta(q_{\max} - q_{||}) \times \text{Im}\{g[q_{||}, \epsilon - \epsilon_b + \hbar\omega(k'_{||})]\}, \quad (12)$$

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

For the system we consider $k_F = 0.23$ a.u., $q_{\max} = 0.1$ a.u., $e_b = 0.76$ eV, and the QW band dispersion $\hbar\omega(k_{||}) = \epsilon_b(k_{||}/k_F)^2$. The calculated dispersion of the e -plasmon excitations is shown in Fig. 4.

The loss of energy for an electron with wave vector $\mathbf{k}'_{||}$, inelastically scattered due to excitation of an ASP to a state

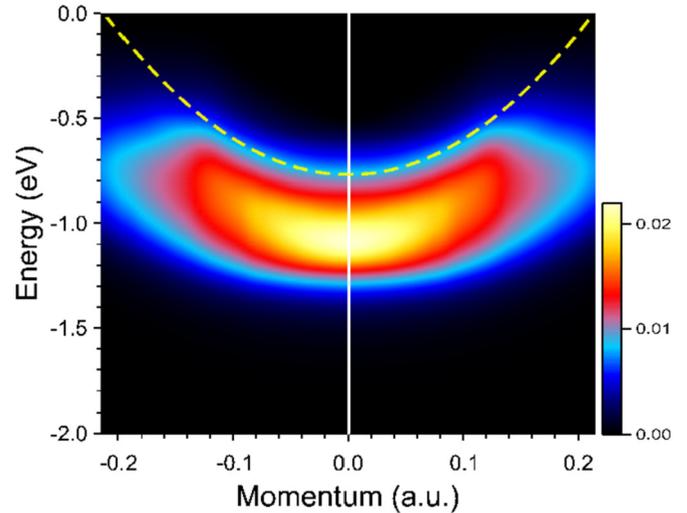


FIG. 4. (Color online) Plasmaron dispersion. The dashed line shows the calculated dispersion of the quantum-well band. The energy scale is relative to the Fermi level. The colored scale gives the rate of the e -plasmon excitation in atomic units (a.u.) for the case $z_0 = 5$ a.u.

$\mathbf{k}_{||} = \mathbf{k}'_{||} + \mathbf{q}_{||}$, is determined by a straight line with the slope c (ASP velocity) drawn from the QW band at $\mathbf{k}'_{||}$ to $\mathbf{k}_{||}$. Due to the fact that the maximum plasmon wave vector q_{\max} is about half the value of the k_F , the e -plasmaron dispersion will essentially follow the shape of the QW band. At the $\bar{\Gamma}$ point, the scattering from the full circle with radius q_{\max} will determine the location of the maximum intensity on the energy axis. For this system with $c = 0.23$ a.u. the maximum is at about 0.4 eV below the bottom of the QW band.

It is interesting to note that the shape of the dispersion of the e -plasmon excitations will depend on the maximum ASP wave vector q_{\max} . In the case that $q_{\max} > k_F$ the dispersion should be more-or-less linear. This case is illustrated by the crossed dashed lines in Fig. 5. Furthermore, in general, if the QW band is parabolic, the crossing point between the dashed lines should appear at an energy twice the binding energy (ϵ_b), as the ASP velocity c (slope of the dashed line) is expected to be close to k_F [22] (the slope of the QW band at the Fermi level).

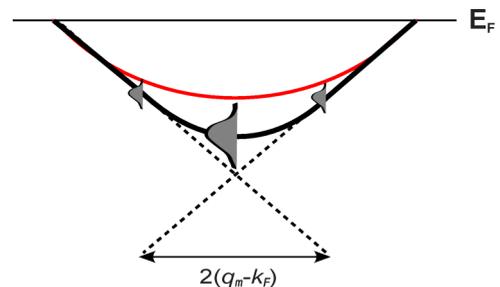


FIG. 5. (Color online) Schematic of the dispersion of the e -plasmon excitation rate. The thin solid red line is the QW band, the thick black line is the dispersion of the e -plasmon excitation rate, and the dashed black line is the expected dispersion if the plasmon cutoff momentum vector $q_{\max} > k_F$.

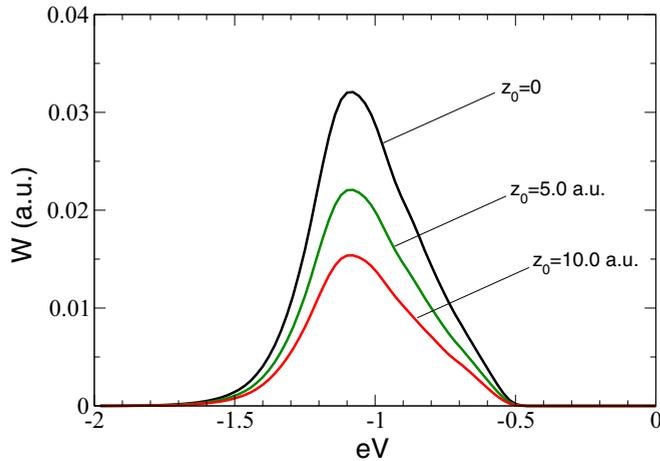


FIG. 6. (Color online) Plasmaron excitation rate at the $\bar{\Gamma}$ point for three different values of z_0 , the distance between the surface, and the position where the ASP excitation takes place.

It is obvious from Eq. (12) that increasing the effective photoelectron-surface distance z_0 where the ASP excitation takes place suppresses the higher- q_{\parallel} contributions, which will reduce the excitation rate of the e plasmaron. This is shown in Fig. 6 for the $\bar{\Gamma}$ point.

IV. SUMMARY AND CONCLUSIONS

Alkali-metal monolayer adsorption on graphite forms *two* quasi-2D systems: one at the top an alkali-metal quantum-well system and one below a doped-graphene type of layer. Thus, we expect that for different types of alkali metals and coverages, it should be possible to design a system with two branches of acoustic surface plasmons, each with its own velocity. In the present study of the p(2 × 2)-K/graphite system, it turns out that only a single ASP branch exists with a

velocity $c = 0.23$ a.u. This result is consistent with the fact that the calculated band structure happens to yield almost identical Fermi velocities for the two 2D systems.

We argue that plasmarons formed due to the direct Coulomb interaction between the photoelectron and its induced electron density, creating ASP excitations, should be considered as a source for loss satellite structure in ARPES for quasi-2D systems. The physics behind this type of excitation, denoted by us as “ e plasmaron”, is different from that of the plasmaron recently reported for graphene [17] and some QW systems [19]. In those cases the picture is that the photohole-plasmon interaction is responsible for the loss structure in the ARPES spectra. We denote these type of hole-related plasmarons as “ h plasmarons.”

In the present study of the system p(2 × 2)-K/graphite system, we calculate the dispersion of the e -plasmaron excitations and analyze in some detail the character of the dispersion. Comparing with reported ARPES experiments [21], it might be that the plasmaron excitations are responsible for the observed high-binding-energy shoulder. A future challenge is to perform a comparative study of the two types of plasmarons to find out (i) which one dominates and (ii) the key parameters for the h plasmarons and the e plasmarons, respectively.

Finally, the e -plasmaron excitations are important to take into account in theoretical studies of different quasi-two-dimensional systems since they reflect an additional channel for excitations of plasmons. This could then increase the photon-plasmon conversion yield which obviously is of interest in the field of applied plasmonics.

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