# Multipole Plasmon Modes at a Metal Surface

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The existence of multipole surface-plasmon modes at simple-metal surfaces is demonstrated both experimentally and theoretically. Inelastic reflection electron-scattering experiments on smooth films of K and Na show loss peaks originating from the ordinary surface plasmon as well as from a higher-energy multipole mode. Microscopic density-functional calculations of the electron-loss function reproduce the energy and momentum dispersion of both of these surface modes. For Al, the multipole mode is shown to be too weak to be observable in electron-loss spectroscopy.

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The electronic excitation spectrum at a metal surface is one of the fundamental topics in surface physics. The surface plasmon, predicted more than thirty years ago by Ritchie,[1] is the best-known example of an electronic eigenmode at the surface of a semi-infinite metal. It has since been observed on many systems. Although the spatial form of the electronic density fluctuation associated with the surface plasmon can be complicated, it has essentially monopole character perpendicular to the surface. Additional electronic surface modes have been predicted for nearly twenty years.[2-6] These modes have been referred to as multipole surface plasmons since their density fluctuation integrates to zero in the direction normal to the surface. While hydrodynamic models can be chosen to give one or several of such higher modes, they are not sufficiently reliable for predictive purposes.[2-4] However, even detailed quantum-mechanical calculations employing the random-phase approximation (RPA) have given inconclusive results. Using a single-step surface-barrier potential, Inglesfield and Wikborg[5] find no multipole surface plasmon for Al. Only for a double-step barrier, designed to simulate alkali-metal overlayers on a Al substrate, does such a mode appear. These results led to the speculation that multipole surface-plasmon modes might be an artifact of the hydrodynamic approximation.[4,6,7] More recently, Dobson and Harris[8] showed that such a mode does in fact exist even for clean Al, if the ground-state electronic properties are described realistically by using the density-functional scheme. However, these authors did not address the question of under what circumstances such a mode might be observable. Despite numerous attempts, no surface excitations corresponding to multipole surface-plasmon modes have so far been observed in electron-loss spectroscopy (ELS). It has been suggested,[9,10] however, that the local-field enhancement observed in photoemission spectra from Al[6,11] is related to the existence of such a mode.

The aim of this Letter is to resolve this long-standing issue in surface physics. We present experimental electron-loss data showing the existence of a multipole surface-plasmon mode at the surfaces of K and Na. We also present calculations which predict such a mode for these low-density alkali metals. The dispersion of the multipole plasmon and of the ordinary surface plasmon are in agreement with experiment. For Al we find that, although a multipole surface plasmon exists, it is too weak to be observable in ELS.

The dispersion of the surface electronic excitations was measured using angle-resolved inelastic electron scattering in the reflection mode. The K (Na) films were grown onto Al(111) by evaporating at 100 K and then annealing to 205 K (240 K). These temperatures were determined by observing the intensity and angular profile of the specularly scattered electron beam for an incident energy of 4 eV. The criteria for the best film were that the reflected intensity be maximized and that the angular profile be narrow. The energy resolution was normally 25 to 35 meV and the angular distribution of the elastic peak was measured to be 2.5°.

Figure 1(a) shows loss spectra from a thick K film. The bottom curve is for collection in the specular direction, where dipole-active excitations dominate the spectrum. A single-loss mode is visible at an energy of 2.61 eV and there is a slight hint of a shoulder or additional peaks at higher binding energy. This dominant peak in the loss spectrum is the surface plasmon at $q=0.16$ Å$^{-1}$ ($q$ is the momentum parallel to the surface). The top curve is for a collection geometry of 10° off the specular direction, where the intensity of the losses is much weaker and non-dipole-active modes can be observed. Three peaks can now be seen. The lowest peak is the surface plasmon shifted to 2.71 eV from the energy of 2.61 eV in the bottom curve, because of the smaller value of $q=0.03$ Å$^{-1}$. The highest-energy peak is the bulk plasmon and the middle peak at 3.2 eV (marked by the

 

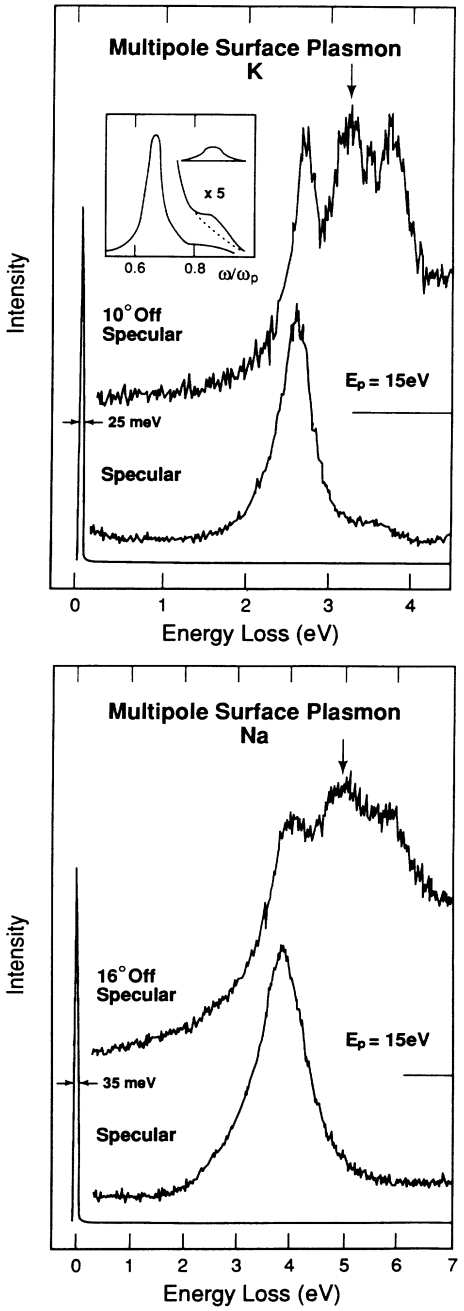


FIG. 1. Electron-energy-loss spectra for (a) K and (b) Na. The bottom curves in (a) and (b) are measurements in the specular direction and the top curves (a) 10° and (b) 16° off of the specular direction. Inset in (a): The calculated loss function $\mathrm{Im}g(q,\omega)$ at $q=0.11$ Å$^{-1}$.

arrow) is the multipole surface plasmon. Figure 1(b) shows a similar set of curves for a thick Na film. A 16° off-specular spectrum was chosen for Na, because the loss features are better defined at this angle.

The probability for creating electronic excitations at the surface of a semi-infinite free-electron gas is, apart from kinematic factors, given by the imaginary part of the reflection amplitude[12]

$$g(q,\omega)=\int dz\, e^{qz}\delta n(q,z,\omega)\,, \tag{1}$$

where $\delta n$ is the self-consistently screened electron density induced at the surface by an external field oscillating at frequency $\omega$. This expression holds in the dipole scattering regime when retardation effects are neglected. The metal is assumed to occupy the half space $z<0$. A typical calculated loss function [$\mathrm{Im}g(q,\omega)$ for real $\omega$] for K is shown in the inset of Fig. 1(a). These results are based on the time-dependent local-density approximation (LDA).[13] The jellium model is used to represent the positive ions of the semi-infinite metal. RPA-type response calculations which neglect the exchange-correlation contributions to the induced potential give similar results.

We have investigated the reflection amplitude $g(q,\omega)$ in the lower half of the complex-frequency plane using a proper analytical continuation[14] and found that the peaks observed in the loss function (real $\omega$) can be traced to the corresponding poles of $g(q,\omega)$ located just below the real axis. For the spectrum shown in the inset of Fig. 1(a), the poles occur at about $(0.67-i0.03)\omega_p$ and $(0.87-i0.03)\omega_p$, respectively. *The analysis of the density fluctuations of these eigenmodes of the semi-infinite electron system shows that the ordinary surface-plasmon peak has monopole character while the upper mode has dipole character (zero total weight).*

Figure 2 shows the comparison of the measured and calculated dispersion of the surface plasmon and the higher-energy multipole plasmon for K and Na. The theoretical results are given for both LDA and RPA response (ground state in LDA) in order to illustrate the effect of exchange and correlation on the dispersion. The vertical bars indicate the uncertainty of the theoretical results which arises from the difficulty of achieving convergence at small $q$ and determining the precise position of the multipole peak. Since effects due to core polarization, etc., are not included in the jellium model, the calculated frequencies were scaled to coincide with the measured surface plasmon at $q=0$. This normalization seems reasonable in view of the fact that the density fluctuations of both modes have their main weight in the same region near the surface. Thus, they are presumably affected in very similar ways by processes that go beyond the jellium model. In the jellium model, the bulk plasmon for a solid with the density of K ($r_s=4.86a_0$) would occur at an energy of 4.40 eV with the corresponding surface plasmon at 3.11 eV while the measured energies are about 12% lower. The measured bulk plasmon for K is observed at 3.80 eV[15] and the energy of our surface plasmon at $q=0$ is 2.74 eV.[16] In the case of Na, the energies of the measured bulk and surface plasmons (5.76 and 3.99 eV, respectively) are about 5% lower than the jellium values.

There is generally good agreement between the experi-

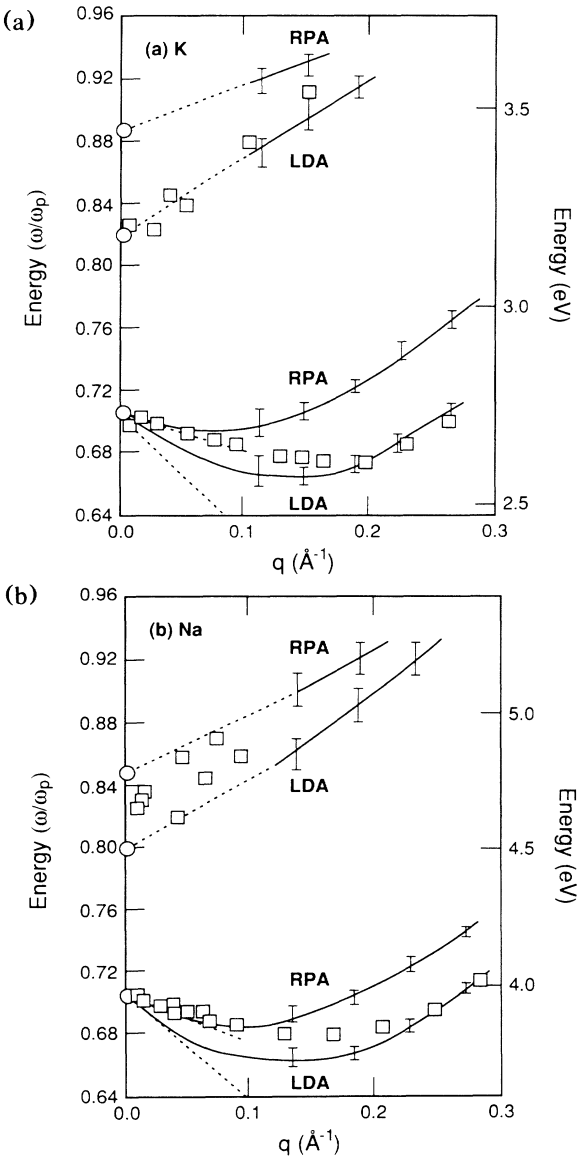


FIG. 2. Momentum dispersion of surface plasmon and multipole plasmon modes for (a) K and (b) Na. The squares are experimental data, the vertical bars denote the results of the LDA and RPA response calculations, the solid lines are only a guide to the eye, the dashed lines are the calculated linear slopes at small $q$ from Eq. (2) with $d(\omega)$ taken from Ref. 17, and the circles denote the $q=0$ limits for both modes (Ref. 17).

ment and theory. The dispersion of the surface plasmon at small $q$ is seen to be negative[16] while the multipole mode displays a positive dispersion. The RPA calculation reproduces the initial slope of the surface plasmon but departs from the data at larger $q$ where the LDA seems to work better. The dispersion of the multipole mode for K is rather well reproduced by the time-dependent density-functional approach, in particular at small $q$.[17] These results suggest that, like in the case of the $q$ dependence of the bulk plasmon,[15] the dispersion of the surface collective modes of low-density alkali metals such as K is influenced significantly by exchange-correlation terms. For Na, the situation is less clear.

To understand the dispersions shown in Fig. 2, it is useful to examine the reflection factor $g(q,\omega)$ in the long-wavelength limit. For $q\rightarrow 0$, one has[6]

$$g(q,\omega)=[1-\epsilon(\omega)^{-1}]/[1+\epsilon(\omega)^{-1}-2qd(\omega)]\,, \quad (2)$$

where $\epsilon(\omega)$ is the Drude dielectric function and $d(\omega)$ is the centroid of the induced density at $q=0$, measured from the edge of the positive background.[6,17,18] Inserting the Drude function into (2), one finds that the frequencies of the eigenmodes of the semi-infinite electron gas are given by the relation

$$\omega=\omega_{sp}[1-qd(\omega)/2]\,, \quad (3)$$

with $\omega_{sp}=\omega_p/\sqrt{2}$. Thus, as long as $d(\omega)$ is small and weakly dependent on $\omega$, the system sustains only the surface-plasmon mode. This mode disperses downward[16] since for metals the efficient screening causes the surface charge to lie in the tails of the equilibrium density, i.e., outside the jellium edge so that $\mathrm{Re}d(\omega_{sp})>0$. Thus, increasing $q$ implies a lower average density in the region of the plasmon density fluctuation and a correspondingly lower frequency. On the other hand, if $d(\omega)$ shows a resonance at some frequency $\omega_r$, it can be shown[10] that $\mathrm{Im}g(q,\omega)$ exhibits a second peak that disperses linearly upwards at small $q$. The dashed lines in Fig. 2 indicate the initial linear dispersion of the surface plasmon and of the multipole plasmon expected from Eq. (2) with $d(\omega)$ taken from Ref. 17. They are seen to be consistent with the dispersions obtained from the full calculation at larger $q$.

It still remains to explain why the multipole mode has not been observed in inelastic electron-scattering experiments from Al ($r_s=2a_0$), while it is believed that the multipole mode is responsible for the local-field enhancement[9,10] seen in the photoemission spectra at $0.8\omega_p$.[11] According to the theoretical results shown in Fig. 2 of Ref. 17, it is clear that in the case of Al the amplitude of the resonance of $d(\omega)$ is too small to lead to a second root in the denominator of Eq. (2) (for real $\omega$). The reason is that the multipole lies too far below the real-$\omega$ axis.[8] At the same time, the damping of the surface plasmon is much larger for high bulk densities. The full width at half maximum of the measured surface plasmon loss at $q=0$ is $0.15\omega_p$, $0.07\omega_p$, and $0.05\omega_p$ for Al, Na, and K, respectively.[19,20] The loss spectra of Al, therefore, show a single surface loss corresponding to the surface plasmon in agreement with experiment. In contrast, the simple metals with lower bulk density such as Na and K show a much stronger local-field enhancement near $\omega\sim 0.8\omega_p$. The nearly singular frequency dependence of $d(\omega)$ for the low-density metals[17] gives a weak but clearly discernible structure in the electron-loss function $\mathrm{Im}g(q,\omega)$ as shown in the inset of Fig. 1(a).

Thus, we now understand why the multipole mode has not been observed previously. First, it has a much weaker dipole-active cross section than the surface plasmon and, consequently, it will be swamped in an inelastic scattering experiment by the surface plasmon unless careful off-specular measurements are made. Second, although detailed density-functional-response calculations show that this mode exists on all simple metal surfaces, only in the case of the low-density alkali metals is it sufficiently strong to produce a separate peak in electron-loss spectra. Third, because of the weaker damping of the surface-plasmon modes in the low-density alkali metals, the multipole loss peak can be easily separated from the ordinary surface plasmon and from the bulk plasmon. There is no inconsistency in claiming that the multipole mode is too weak and broad to be observed in an elastic electron-scattering experiment for Al, yet invoking this mode as the origin of the local-field enhancement seen in the photoemission spectra from Al. Light does not couple to the surface-plasmon mode for clean flat surfaces (in contrast to the multipole mode[21]) and, consequently, the surface-plasmon mode is removed from these spectra[11] leaving the multipole mode observable.

We want to emphasize that the term "multipole surface plasmon" applies, strictly speaking, only to the singularities of $g(q,\omega)$ in the lower half of the complex-frequency plane. Along the real-$\omega$ axis, the tails of these poles lead to peaks in the loss function which are more or less strongly broadened due to decay into electron-hole pairs. It is therefore equally justified to refer to these excitations as resonances in the electron-hole–pair spectrum. Thus, the electron fluctuation associated with these loss features at real $\omega$ does no longer have purely dipolar character. It is also important to keep in mind that, whether or not these peaks are actually observable, depends crucially on the nature of the external probe.

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