Classical Size Dependence of the Work Function of Small Metallic Spheres

I wish to point out that the size variation of the photoelectric threshold for ultrafine Ag particles observed by Schmidt-Ott, Schurtenberger, and Siegmann[1] has a simple, quantitative classical interpretation.

It is known that the work function, the energy required to remove an electron from bulk metal to infinity, has as one of its constituents the work done against the image force,[2] which is the principal interaction beyond a few angstroms above the surface. It is thus important to note that the image potential for a metallic (infinitely conducting) *sphere* differs considerably from that of a *plane.* For the planar case[3]

$$\varphi_{\mathrm{im}}{}^{\mathrm{plane}} = \frac{-q^2}{4x} \quad (x > 0), \tag{1}$$

where x is the distance of the test charge q above the surface. For a metal sphere[3] (R = sphere radius)

$$\varphi_{\mathrm{im}}{}^{\mathrm{sphere}} = \frac{-q^2R^3}{2r^2(r^2-R^2)} \quad (r > R). \tag{2}$$

For $r/R = 1+\delta$ ($\delta \ll 1$), Eq. (2) coincides with the planar case with $x = R\delta$.

Since φ is a *potential*, the difference in work required to remove an electron to infinity from just outside a metal sphere and from a metal plane is

$$\lim_{\delta \to 0^+} \frac{-e^2}{2R[(1+\delta)^2-1]}\,\frac{1}{(1+\delta)^2} - \left(\frac{-e^2}{4R\delta}\right) = \frac{5}{8}\,\frac{e^2}{R}. \tag{3}$$

Hence the work function for a neutral metal sphere will be *reduced* by this amount relative to the planar value. The attraction between the liberated photoelectron and the charge $+e$ *remaining* on an isolated sphere (which may be taken to reside at its center[4]), however, gives rise to an additive energy $-e^2/R$ which will, of course, *increase* the work function. Taken together

$$W(R) = W_\infty + \frac{3}{8}\,\frac{e^2}{R} = W_\infty + \frac{5.40}{R(\text{Å})}\ \text{eV}, \tag{4}$$

where W_∞ is the work function of the planar metal. There is no plane "charging energy" ($R = \infty$).

Probably because impurities are concentrated near the surface because of heating of the wire used to produce the small particles, its photothreshold is not directly comparable to that of the small particles.[5] Instead, one may use for W_∞ a tabulated value of the average work function for bulk Ag, 4.30 eV.[6] Determining W_∞ *by fit* [using Eq. (4)] to the three *small particle* data of Schmidt-Ott, Schurtenberger, and Siegmann, I find

$$W(R) = 4.37 + 5.40/R(\text{Å})\ \text{eV}. \tag{5}$$

[The data points agree to within 0.01 eV as to W_∞ and fall on Eq. (5) to within 0.01 eV.] Moreover, 4.37 differs by less than 2% from the tabulated value of W_∞ above, suggesting that the particles are quite pure.

I conclude that the size dependence of the work function of small metal spheres is in excellent quantitative agreement with classical image-potential expectations. Since the photothreshold $W(R)$ is well above the surface plasmon in small Ag spheres, it seems unlikely, however, that the mechanisms invoked to explain the giant Raman scattering observed for molecules adsorbed on pitted Ag surfaces[7] can explain the photoyield enhancement.

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Note added.—Equation (4) has been previously obtained by Smith.[8] I thank H. C. Siegmann for pointing out this work.

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