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Enormous Yield of Photoelectrons from Small Particles

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A new ac bridge technique allows detailed photoelectric studies on very small particles suspended in gases. The photoelectric yield Y near threshold Φ still follows the Fowler-Nordheim law $Y = c(h\nu - \Phi)^2$; yet c is generally much larger compared to surfaces of extended solids. For Ag particles of radius 20 Å in an airlike mixture of N_2 and O_2, $c \simeq 100c_0$, where c_0 applies to a macroscopic Ag surface in the same environment.

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The purpose of this Letter is to report on a large enhancement of the yield Y of photoelectrons per incident photon if ultrafine particles with radii $R \leq 50$ Å are chosen as photoemitters. The results were obtained with Ag and WO_3 by use of a novel technique in which the density Z of the particles does not have to be known.

The particles are suspended in an N_2-O_2 mixture similar to air. The photoelectric size effect to be reported here has wide implications including photoemission from interstellar dust grains by starlight,[1] atmospheric electricity,[2] nucleation,[3] and smog photochemistry,[3,4] simply because photoemission from small particles has been underestimated so far. It also may become the physical basis for characterizing and measuring very small particles suspended in gases.

For the determination of Y and the particle radius R, the aerosol is illuminated with monochromatic light from a Xe high-pressure arc and the conductivity arising from photoelectron emission by the particles is measured. For this photoconductivity measurement an alternating electric field (amplitude, 30 V/cm; frequency, 90 s^{-1}) is applied to the aerosol in two cylindrical condensers, one of which is exposed to uv light. Here, an in-phase current component is caused by the oscillatory motions of the charge carriers produced by photoemission.[5] The differential conductivity in the two condensers is measured in an ac bridge circuit by means of a phase-sensitive amplifier.[5] In this way, the capacitive component, typically 10^6 times higher than the photoconductivity, can be suppressed and the aerosol conductivity arising from ionization by cosmic rays and natural radioactivity is eliminated.

Aerosol photoconductivity Σ arises from the negative small ions formed by the photoelectrons[6] and the particles left behind with a positive charge. With ultrafine particles ($R \lesssim 30$ Å), small ion reattachment is negligible.[7] Multiple photoelectric particle charging can also be neglected with the low photon energies applied here, because of the strong Coulomb attraction between a doubly charged particle and the second photoelectron. A typical time dependence of Σ in an aerosol exposed to ultraviolet light at $t \geqslant 0$ is shown in Fig. 1(a). The interpretation is simplest when the radiation is removed at t_m, where Σ reaches a maximum.

Σ is governed mainly by the negative small ions formed out of the photoelectrons (concentration n) due to their larger mobility compared to the charged particles. Therefore, Σ reaches the maximum when $dn/dt = 0$, i.e., when the photoelectric emission rate equals the rate of small ion loss to the electrode. The left-hand side of the following equation represents the emission rate at t_m and the right-hand side represents the loss rate at t_m. The latter is the initial slope of n when the light is removed. One obtains

$$j\sigma Y Z^0(t_m) = [\,dn(t_m)/dt\,]_{j=0}\,. \tag{1}$$

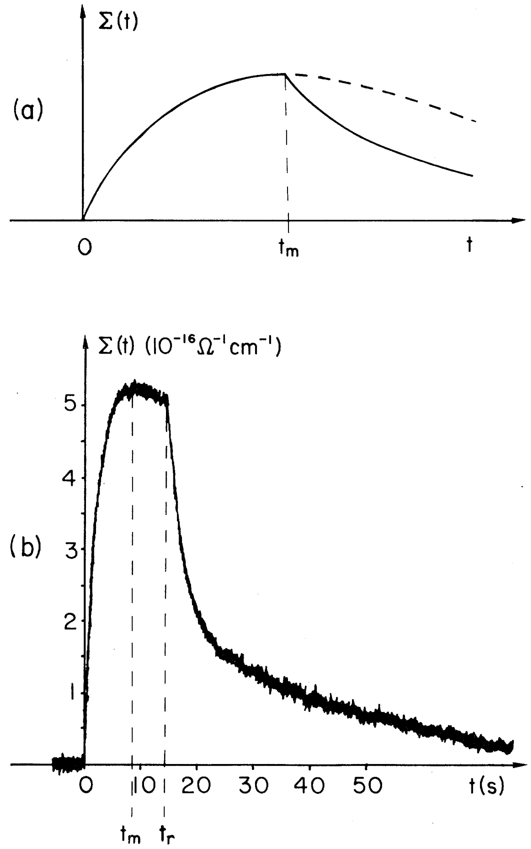

FIG. 1. Time dependence of aerosol photoconductivity Σ. Light is applied at $t = 0$. (a) Typical curve. Light removed at t_m. Dashed line: $\Sigma(t)$, as expected for continuous illumination. (b) Example of a measurement with Ag particles of radius $R = 20$ Å. Light removed at t_r.

σ is the geometrical particle cross section (πR^2) and Z^0 the concentration of neutral particles. The reduction rate of neutral particles by photoelectrical charging is equal to the photoemission rate:

$$-dZ^0/dt = j\,\sigma Y Z^0(t)\,. \tag{2}$$

This results in an exponential decay for $Z^0(t)$.

Substituting Z^0 in (1) and considering that

$$j\,\sigma Y Z^0(0) = dn(0)/dt \tag{3}$$

leads to

$$\sigma Y = \frac{1}{j t_m} \ln\left[-\frac{dn(t_m)}{dt}\bigg|_{j=0}\left(\frac{dn(0)}{dt}\right)^{-1}\right], \tag{4}$$

where

$$\frac{dn(t_m)}{dt}\bigg|_{j=0}\left(\frac{dn(0)}{dt}\right)^{-1} = \frac{d\Sigma(t_m)}{dt}\bigg|_{j=0}\left(\frac{d\Sigma(0)}{dt}\right)^{-1}$$

and t_m are taken from the measured $\Sigma(t)$, an example of which is shown in Fig. 1(a).

The particle cross section $\sigma = \pi R^2$ is obtained in two independent ways through the particle diffusion loss to the electrodes and the contribution Σ_p of the particles to conductivity. After exposure ($t > t_m$), the conductivity decays according to the diffusion losses of the charge carriers [Fig. 1(b)], and is therefore a superposition of two exponential decays, the decay rates β_s and β_p being proportional to the diffusion constants of small ions and particles, respectively. Since $\beta_s \gg \beta_p$, the contributions of small ions and particles are well separable and β_s and β_p as well as the conductivity $\Sigma_p(t)$ produced by the particles alone can be determined. Since β_s and β_p are proportional to the corresponding diffusion constants[8] or mobilities b_s and b_p,

$$b_p = b_s \beta_p / \beta_s, \tag{5}$$

where $1 \leqslant b_s \leqslant 2$ cm^2/V·sec in an airlike gas mixture.[6] Furthermore,

$$\Sigma_p = eZ^+ b_p\,. \tag{6}$$

This also yields b_p since the concentration of charged particles, Z^+, can be calculated from the photoemission rate.

Ultrafine Ag particles were prepared by heating a Ag wire in a N_2 flow at normal pressure. O_2 was continuously mixed to the aerosol to form a 4:1 N_2-O_2 mixture. The gases were dried by cooling to −80 °C. The aerosol was neutralized by means of a ^{85}Kr radioactive source. The particle size was varied with the wire temperature. A commercial electrical aerosol analyzer[9] confirmed the absence of particles with radii larger than 40 Å.

The steady-state photoconductivity in a flowing aerosol is proportional to Y. This allows a convenient relative determination of the yield. The absolute calibration is done from $\Sigma(t)$ according to (4).

The Fowler-Nordheim law,[10]

$$Y(h\nu) = c(h\nu - \varphi)^2, \tag{7}$$

as valid for macroscopic metal surfaces, was found to apply in the photon energy range $h\nu - \varphi \lesssim 1.5$ eV for particles of Ag, Au, MoO_3, and WO_3 with various particle sizes.

Table I shows the results obtained with Ag particles and the comparison to the yield Y from a semi-infinite plane, which is the wire from which the particles were produced by evaporation. After heating the wire in N_2, it was exposed to the same N_2-O_2 mixture as the particles. For the particle-radius determination, the diffusion loss method [Eq. (5)] seemed more reliable and was therefore applied. The particle conductivity measurement, however, yielded identical results with $b_s \approx 1.3$ $cm^2/V \cdot sec$ in Eq. (6).

A drastic increase of c with decreasing particle radius and an enhancement as large as 110 for the 20-Å particles in comparison with the macroscopic surface demonstrate a pronounced size effect. An even greater yield enhancement has been observed for an aerosol of particles with a mean radius of 50 Å produced from a heated WO_3 surface. Measurements on various other aerosols with various size spectra also point to high photoelectric yields. The increase of the photothreshold φ in Table I with decreasing R is a result of the Coulomb attraction between particle and photoelectron. Subtracting the Coulomb enhancement $e^2/4\pi\epsilon_0 R$ of the photothreshold from φ, leads to $\varphi_0 \approx 4$ eV for the Ag aerosols. The fact that the wire threshold is considerably higher indicates that the crystal orientations at the surface and/or the adsorbate situation of particles and wire are different. This can, however, not explain the yield enhancement, since a dipole layer caused by surface adsorbates basically has the effect of a φ change only. The influence of an adsorbate on the particles was demonstrated qualitatively by adding small amounts of H_2O vapor to the aerosol. A φ increase for Ag particles and a φ decrease for WO_3 particles both in the order of 0.1 eV resulted, while c in (7) remained constant.

TABLE I. Radius R, photoelectric threshold φ, and photoemission constant c [Eq. (7)] of Ag particles and macroscopic surface.

	R (Å)	φ (eV)	c
Particle	30	4.55	1.8×10^{-3}
	27	4.57	3.9×10^{-3}
	20	4.65	8.9×10^{-3}
Macroscopic surface	∞	4.90	7.3×10^{-5}

To explain the photoelectric yield enhancement it is first considered that the phase space for escape of photoexcited electrons is larger in a spherical photoemitter compared to a plane if R is comparable to the elastic mean free path λ_e of excited electrons. A calculation of the escape probability of photoelectrons from a sphere relative to a semi-infinite solid[11] shows that enhancement factors up to 4 are possible under the assumptions of a homogeneous source strength/volume for excited electrons with $h\nu$ close to φ and an inelastic collision attenuation according to $\exp(-x/\lambda_e)$. The phase-space enhancement was found to be independent of $h\nu - \varphi$, so that the validity of the Fowler-Nordheim law is retained for small particles in agreement with the present observations. Yet this type of enhancement is definitely not large enough to understand the present data. We conclude that it must have to do with the special ways in which radiation is absorbed in small particles.

The particle dimension is much smaller than the uncertainty field of the photon ($\lambda \approx 2300$ Å). This fact must cause a difference in the absorption of radiation. A similar observation has been made in the Raman scattering from molecules adsorbed on Ag surfaces. Enhancement factors of up to 10^6 have been reported when the Ag surface was microscopically rough.[12] The present observation of an enhanced photoemission may facilitate the explanation of the surface enhanced Raman effect. If the radiation is absorbed closer to the surface in a small particle which is consistent with the model of Burstein, Chen, and Lundquist,[13] then the enhanced photoemission can be understood readily. Levinson, Plummer, and Feibelman[14] have shown that photoionization cross sections are enhanced drastically in the region of spatially varying photon fields near a metal surface.

At present, we use the large photoelectric yield to obtain new information on ultrafine particles and their surfaces in the atmosphere.[15] An apparatus employing photoelectric charging of atmospheric aerosols with subsequent analysis of the electrical mobility of the charged particles is being developed. Of special interest to studies on artificial weather modification seems to be the fact that layers of water adsorbed on the surface of the particles can be detected by the induced change in photoelectric work function.

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Giant Raman Scattering by Molecules at Metal-Island Films

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A major part of the giant Raman scattering by adsorbed molecules on a Ag-island film is shown to be due to the large increase in the electric field at the molecules and to the large electric dipole moment of the molecule–metal-island complex that result from the excitation of the transverse collective electron resonance of the film.

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It is now well established that surface roughness on a submicroscopic scale plays a crucial role in the giant enhancement of the Raman-scattering (RS) molecules adsorbed on an Ag electrode.[1,2] Creighton, Blatchford, and Albrecht[3] have suggested, on the basis of their studies of the enhanced RS by pyridine adsorbed on Ag and Au aqueous sol particles, that the enhancement was due to the excitation of "localized" surface plasmons. They proposed that the molecular vibrations modulate the very large polarizability of the metal particles. A similar interpretation was proposed independently by Moskovits,[4] who suggested that the enhancement and the wavelength dependence of the RS by pyridine adsorbed on a Ag electrode is due to the excitation of the collective electron resonance of submicroscopic bumps on the Ag surface. However, apart from an analogy to the resonance enhancement of the RS by ligands attached to metal atoms, he gave no explanation of the magnitude of the enhancement. Chen and co-workers[1,5] have also focused on the role played by the collective electron resonances of the rough Ag surface. They suggested that the excitation of the transverse collective resonance enhances the incident field at the mol-