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Research Report

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R. Berndt[a], H.-V. Roy[a], C. Monreal[b], N. Lorente[b], P. Fayet[a], P. Apell[c], J.K. Gimzewski[d] and W.-D. Schneider[a]

[a]Université de Lausanne
1015 Lausanne
Switzerland

[b]Universidad Autónoma de Madrid
28049 Madrid
Spain

[c]Chalmers University of Technology
41296 Göteborg
Sweden

[d]IBM Research Division
Zurich Research Laboratory
8803 Rüschlikon
Switzerland

IBM Research Division
Almaden · T.J. Watson · Tokyo · Zurich

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[a] *Université de Lausanne, 1015 Lausanne, Switzerland*

[b] *Universidad Autónoma de Madrid, 28049 Madrid, Spain*

[c] *Chalmers University of Technology, 41296 Göteborg, Sweden*

[d] *IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland*

Abstract: Emission of visible photons was observed as mass selected clusters of Ag_n^+, Pt_n^+, and Pd_n^+ ($n =$ 1...5) impinge on surfaces of Ag and graphite at low kinetic energies (~8 eV). The emission intensities display distinct cluster-size effects for each of the cluster materials. The observations are interpreted in terms of resonant neutralization and radiative capture of electrons tunneling at nanometer distances. The photon emission process is shown to depend sensitively on the proximal evolution of the ionization energy of the cluster as it approaches the surface.

Clusters of metal atoms are the subject of intense basic and applied research [1]. The evolution of the physical properties from an atom to those of a solid is of fundamental interest. Moreover, clusters supported by suitable substrates have attractive catalytic properties or serve as model catalysts [2]. In this context low-energy deposition of clusters has been used to study cluster-size effects [3–5]. Nevertheless, little is known about the physics of the cluster-surface interactions such as tunneling, charge transfer, electromagnetic coupling, and the evolution of the electronic structure and excitations. These phenomena all occur at nanometer and sub-nanometer proximity. While theoretically the evolution of the geometry of a cluster impinging on a surface has been investigated by molecular-dynamics simulations [6], experimental data is scant in this crucial proximal region. Here we report the first observation of photon emission from positively charged, mass-selected clusters which impinge on surfaces. The photon emission represents a new probe which *selectively provides a signature of cluster proximity to a surface*. The intensity of the observed emission depends strongly on both the chemical identity and the size of the clusters. We propose that photon emission occurs by means of radiative electron tunneling from the surface to the cluster (Fig. 1). Both experimentally and by model calculations the photon emission is shown to exhibit a sensitive dependency on the evolution of the ionization energy of the cluster as it approaches the surface.

Interestingly, the present experiment is a quantum sized analogue to photon emission from metals in the scanning tunneling microscope (STM) [7]. Here the tip of the STM and its bias voltage are replaced by a charged metal cluster the size of which can be selected on an atom by atom level (cf. Fig. 1). As in the STM experiment, enhancement effects in the photon emission are expected to occur due to plasmon resonances for very large clusters. We demonstrate that small clusters (1...5 atoms) exhibit a dramatically different behavior.

Phenomena related to the present experiment are also observed during chemisorption on metal surfaces. In this case the emission of photons [8–10] and electrons [9] has been reported and analyzed in terms of non-adiabatic electronic processes [11,12]. Blackbody radiation has been observed from free Niobium clusters upon oxidation [13]. We note that light emission from ions impinging on solids has been the subject of much interest [14].

Surfaces of polycrystalline silver or highly oriented pyrolytic graphite (HOPG) were irradiated at an incident angle of $\sim 30°$ with respect to the surface normal with beams of Ag_n^+, Pt_n^+, and Pd_n^+ ($n = 1...5$) using a mass selected cluster source described in Ref. [15]. The coverage of the surface with cluster material remained well below one monolayer during the experiment. After a flight time of ~ 1ms which ensures relaxation to the electronic ground state the clusters reach the sample with a kinetic energy of (8 ± 6)eV. The photons emitted from the sample surface were collected with a lens placed at an angle of $\sim 90°$ with respect to the cluster beam in its plane of incidence. The photons were then transmitted through a viewport and detected outside the vacuum vessel by a photomultiplier. The detection equipment was sensitive to photons in the wavelength range 200 nm $< \lambda <$ 800 nm emitted into a solid angle of ~ 0.1 steradian. The ratio of the number of photons detected versus the number of photons emitted under the solid angle seen by the setup is estimated to be 5% at a photon energy of 2 eV.

To suppress the photon background due to light emission from the cluster source the beam was deflected by 90° and a light trap was installed. The ion-optical components were coated with carbon. Defocussing by the deflector resulted in a beam diameter exceeding the sample size. Consequently, variations of the cluster beam profile insignificantly affected the number of detected photons. We further verified that the size effects of the photon intensity were also observed without the deflector albeit with poorer signal-to-noise ratios.

For each cluster size the photon intensity was measured as a function of cluster ion beam current to determine the photon yield (counts per incident charge). Figure 2 shows data for Ag_2^+ impinging onto polycrystalline Ag. The photon intensity bears a linear relationship with

the sample current clearly implying that the emission process involves single clusters. The photon yields measured for Ag clusters impinging onto Ag and HOPG surfaces have been compiled in Fig. 3a. A distinctive cluster size effect is readily observed for both substrate materials: Maxima in yield occur for even-sized Ag clusters. Dimers show by far the highest yield. While the data from many different experimental runs showed identical relative yields the absolute photon intensities exhibited some variability. As a consequence, below we will discuss relative yields as a function of cluster size only. Data for Pd and Pt clusters impinging on polycrystalline Ag are also summarized in Fig. 3. The evolution of the yields with cluster size are distinctly and significantly different. Most notably, in comparison with Ag the emission is minimal for dimers of Pt and Pd whereas Ag exhibits a dominant maximum in the cluster size progression. The clear odd-even effect observed for Ag is absent for Pt and Pd.
Some immediate consequences may be deduced from the above data. First, a mechanism which would directly involve the kinetic energy of the clusters can be discarded. Since the experiment is performed at approximately constant incidence energy one would expect monotonous and similar size dependencies of the photon emission for all cluster materials in contradiction to the observations of Fig. 3. Second, another possible mechanism is luminescence inside the metal due to hot holes left by electrons tunneling into the cluster. The efficiency of this process is estimated from Mooradian's measurements of the photoluminescence yield which indicate a recombination probability of 10^{-10} for Cu and Au [16]. For Ag a similar yield is expected. Thus, the luminescence intensity due to hot holes is 2 – 3 orders of magnitude lower than our experimental value permitting us to discard this mechanism. Third, the striking size effects clearly point to the clusters themselves as the determining factor for the observed behavior. For Ag clusters, the ionization energy is known to exhibit a pronounced odd-even size effect [17]. Therefore, the observed odd-even variation of the photon emission intensities hints to a mechanism which involves the lowest unoccupied cluster level. The exciting possibility, that is consistent with all the experimental observations, is that photon emission occurs by radiative neutralization of the clusters as electrons tunnel from the substrate.
To understand and evaluate this process we performed calculations of the probabilities of photon emission due to radiative tunneling and resonant neutralization starting from the model of Nørskov, Newns, and Lundquist [11]. Briefly, the calculation is performed as follows. The probability of photon emission from a cluster at a nanometer distance z from the metal surface is $1/\tau_{ph}(z)$. The fraction of the initial ions surviving as ions at z is $n_+(z)$. The total number of emitted photons per impinging ion, γ, can be obtained by adding all the contributions along the ion trajectory as

$$\gamma = \int \frac{dz}{v} \frac{1}{\tau_{ph}(z)} n_+(z). \tag{1}$$

where v is the ion velocity.
The rate for photon emission is given by a golden-rule expression with the matrix element for the electromagnetic coupling between the wavefunction of the cluster ψ_a of energy $E_a(z)$ and the wavefunction of the metal electron $\psi_{\mathbf{k}}$ with the energy $E_{\mathbf{k}}$. For the vector potential the classical version of the electromagnetic field near a planar metal surface is used. The Ag substrate is treated in the jellium model with $r_s = 3\ au$. The wave functions $\psi_{\mathbf{k}}$ are solutions of a Jennings potential [18] corresponding to a Fermi energy of 5.3 eV and a work function of 4.3 eV. The wave functions ψ_a of the different clusters are approximated firstly with a hydrogen model where all cluster sizes can be treated.
In proximity with the surface the cluster levels shift and broaden mainly due to resonant neutralization (RN) which is the dominant neutralization channel when available [19]. For even the simplest system of an H atom in front of a jellium-like surface, calculation of the

energy levels and their widths is complicated [20]. Consequently, we use Gadzuk's expression to approximate the level widths of the clusters [21]:

$$\frac{1}{\tau_{RN}}(z) = 2\pi \sum_{\mathbf{k}<k_f} | < \psi_{\mathbf{k}} | \frac{Z_{eff}}{|\mathbf{r}-\mathbf{z}|} | \psi_a > |^2 \delta(E_{\mathbf{k}} - E_a(z)), \tag{2}$$

where Z_{eff} is the effective charge of the ion in the hydrogenic model. Then, the number of ions at the distance z is given by the master equation

$$\frac{dn_+(z)}{dz} = \frac{1}{v\tau_{RN}(z)} n_+(z). \tag{3}$$

For illustrative purposes we study two limiting cases of the shift of the energy levels. We assume first that the energy level follows the classical image potential

$$E_a(z) = E_a(z=\infty) + \frac{1}{4(z-z_0)}, \tag{4}$$

z_0 being the position of the image plane and, second, that the energy level does not change with distance, $E_a(z) = E_a(z=\infty)$. The former case means that the cluster ion state is localized to a point charge which appears reasonable for smaller clusters. A weaker effect may be expected for larger clusters which average over a larger region of the surface potential. This effect is represented by the latter case. In support of the "weakening of the image shift", for H the 1 s level follows Eq. 4 whereas the more extended $n=2$ levels show a smaller shift [20]. Figure 4 shows the photon yield for Ag_n^+ clusters impinging on a Ag substrate with a kinetic energy of 8eV as calculated using Eq. 1 with the ionization energies of Ag clusters from Ref. [17]. For the present purposes it is enough to take the cluster velovity v as constant. The results of our calculations clearly follow the experimental trend. The ionization energy of the clusters, $|E_a(z=\infty)|$, determines this behavior. As in STM, most of the photons are emitted when electrons near the Fermi level tunnel radiatively. This occurs at a nanometer distance z_m where the number of ionized clusters is reduced to about 1/2 due to the RN process. The distance z_m is related to the ionization energy: i.e. the larger $|E_a(z=\infty)|$ is, the closer the ion gets to the surface before being neutralized by the RN process. Since a smaller value of z_m also implies a larger probability of emitting photons the photon yield follows the ionization energy in both calculations. This also explains that Ag and HOPG substrates produce similar photon yields owing to their similar work functions and band structures.
The calculated yield without level shift is higher than with the image shift. This is because in the former case the ions get closer to the surface and more photons are emitted in a wider energy range. Moreover, the level shifts strongly affect the ratio of yields for different cluster sizes. The image shift of Eq. 4 decreases the value of $|E_a(z_m)|$ and, in turn, the energy of the emitted photons. Experimentally this manifests itself by lower count rates for cluster sizes $n=3,4$ and 5, due to the cut-off of the photomultiplier response at energies below ~ 1.5 eV. The ratio 1:2:1 of the experimental yields for $n=3,4$ and 5 is reproduced by our calculation without image shift. On the other hand, the experimental ratio of 100:1 for $n=1$ and 2 lies in between both calculations. This comparison of the calculation with the experiment points towards a weakening of the image shift for increasing cluster size.
In the case of Ag_1 we further improved upon the hydrogenic model by using a Hartree-Fock wave function in Eq. 2 and in the golden rule expression while keeping the same image shift terms. Here the photon yield increases by a factor of 3. The Hartree-Fock wave function is more extended than the hydrogenic one and has a larger overlap with the metal electrons. This suggests that the larger photon yield of Ag_2 compared to Ag_1 in the experiment can

be ascribed to a more extended wave function for Ag_2 [22] together with a weakening of the image shift effect.

For the Hartree-Fock treatment of Ag_1, the yield is only one order of magnitude below the experimental value. The remaining deviation may be due to the lowering of the barrier seen by the metal electrons due to the ion potential. This effect has been invoked for Auger neutralization of slow He^+ ions [23]. It causes the metallic wave functions to have a much slower decay outside the metal thus increasing the overlap with the atom.

In summary, we report the first observation of photon emission during the interaction of ionized cluster beams with surfaces. The photon intensities were shown to quantitatively depend on the cluster sizes and their chemical identity. Model calculations indicate that the observed photon emission is predominantly due to radiative neutralization by inelastic tunneling of electrons. The emission is found to be a sensitive probe of the position of the cluster ionization level which is modified with respect to a free cluster by the electronic mixing with the target surface at nanometer distances. We propose that the photon emission may be used to characterize cluster-surface interactions at (sub)nanometer distances where charge transfer and electronic excitations occur.

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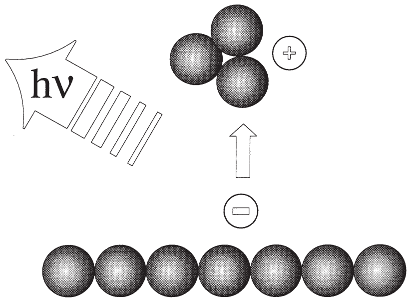

FIG. 1. Schematic diagram of a positively charged, three-atom cluster which approaches a surface. Neutralization by an electron which tunnels inelastically from the surface to the cluster can lead to neutralization and the emission of a photon. This experiment represents a quantum sized analogue to photon emission from metals in the scanning tunneling microscope. The tip of the STM and its bias voltage are replaced by a charged metal cluster.

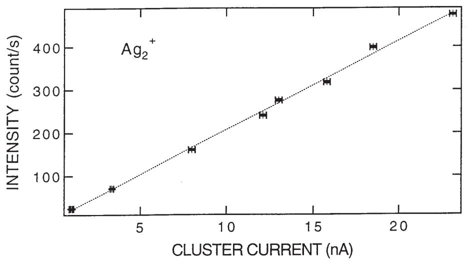

FIG. 2. Photon emission intensity detected from Ag_2^+ clusters impinging onto a polycrystalline Ag versus cluster current. No background photon intensity has been subtracted.

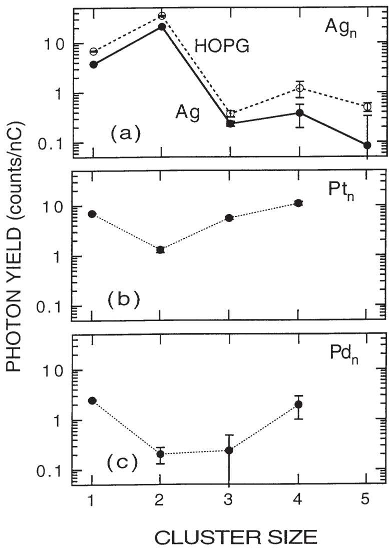

FIG. 3. Experimentally observed photon intensities versus cluster size for Ag_n^+ impinging onto Ag and HOPG (a), and Pt_n^+ (b), Pd_n^+ (c) impinging onto Ag.

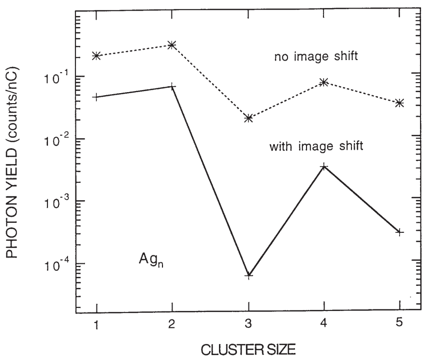

FIG. 4. Photon intensities for Ag_n^+ impinging onto Ag calculated in the hydrogenic approximation. The spectral response of the detection set-up and the solid angle detected have been included in the model.