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Size-dependent light emission from mass-selected clusters

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Abstract. The emission of photons in the visible wavelength range from mass-selected Ag_n^+, Cu_n^+, Pt_n^+ and Pd_n^+ ($n = 1 \ldots 5$) clusters is observed. Photons are detected $\approx 10^{-4}$ s after the cluster generation in a sputter source. The emission intensities display distinct variations with cluster size and material. The observations are interpreted in terms of the decay of metastable states which are excited during the high-energy sputtering process used for the generation of these clusters.

PACS. 32.50.+d Fluorescence, phosphorescence (including quenching) – 36.40.-c Atomic and molecular clusters

1 Introduction

Clusters of metal atoms are the subject of intense basic and applied research because they encompass the evolution of the physical and chemical properties of an atom to those of a solid [1]. Gas-phase experiments of size-selected metal clusters [2] have shown large size-dependencies in the ionization potential (IP) with a distinct shell structure for alkaline [3,4], Ag [5,6] and Cu clusters [5]. Moreover, clusters supported on suitable substrates have attracted considerably interest as model catalysts [7,8]. Low-energy deposition of clusters has been used to study cluster-size effects [7–14]. Here we report on the observation of positively charged, mass-selected clusters emitting photons from radiative deexcitation of Rydberg states [15]. We find the intensity of the observed emission to depend on both the chemical identity and the size of the clusters.

While the results presented here are unique, other photon emission observations have been made [16–21]. Upon oxidation, black-body radiation in the 350 nm ... 750 nm range has been observed for free Nb_n ($n \approx 260$) clusters with a broad size-distribution, as chemical reaction of these Nb clusters with O_2 leads to a vibrational energy increase [16]. Recently photon emission of laser induced optical transitions in the 440 nm ... 830 nm range for W_n, Nb_n and Hf_n ($n \approx 150 \ldots 550$) clusters have also been interpreted in terms of black-body radiation [17]. The same model was evoked for optical emission studies of carbon particles produced from a laser vaporization cluster source [18] and laser desorbed C_{60} [19]. Visible and infrared luminescence was observed from free Xe cluster ions and is assigned to radiative transitions in the atomic ion [20]. Chemiluminescence of Cu and Ag clusters in noble gas matrices was also reported. Clusters formed by agglomeration are excited to intermediate energy states with short lifetimes ($10^{-8} \ldots 10^{-9}$ s). Visible light is then emitted during the relaxation process [21]. Initially, our experiments were aiming at detecting photon emission from clusters during their deposition on surfaces [22]. In the present apparatus this effect is masked by the light emission reported here.

2 Experimental

In the present experiment, beams of mass-selected Ag_n^+, Cu_n^+, Pt_n^+ and Pd_n^+ ($n = 1 \ldots 5$) clusters with kinetic energies between 10 ± 5 eV and 35 ± 5 eV are produced by a sputter cluster source [8–14]. Light emission of the mass-selected clusters is then analyzed with a photon detection setup at a distance of ≈ 1 m from the cluster source, *i.e.* after a flight time of $\approx 10^{-4}$ s (Fig. 1). Measurements are made in a high vacuum chamber with a base pressure of 1.5×10^{-8} Torr. The emitted photons are collected with a lens which is focussed to the cluster beam axis. They are then transmitted through a viewport and detected by a photomultiplier (Hamamatsu R2949). The detection equipment is sensitive to photons in the wavelength range 200 nm $< \lambda <$ 800 nm emitted into a solid angle of ≈ 0.3 steradian. Spectra over the whole available wavelength range could not be recorded due to low

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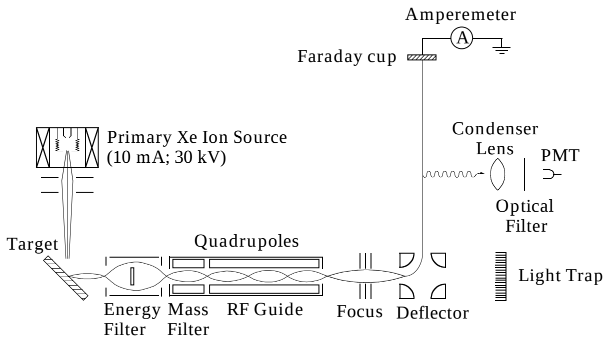

Fig. 1. Schematic view of the experimental setup for the production and size-selection of the clusters collected on a Faraday cup. The emitted photons are focussed by an optical lens and detected with a photomultiplier tube (PMT).

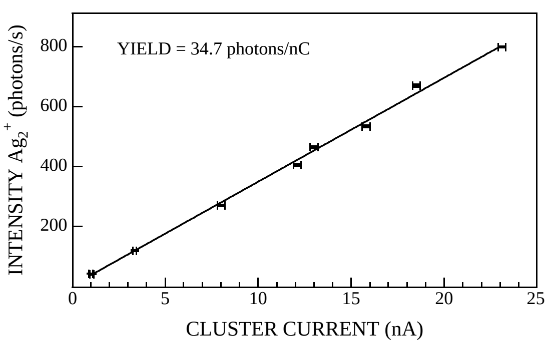

Fig. 2. Total photon emission intensity detected from Ag_2^+ *versus* cluster current. From the slope of this curve, we obtain the total photon yield. The background defined as the intensity for 0 nA is negligible (2 photons/s).

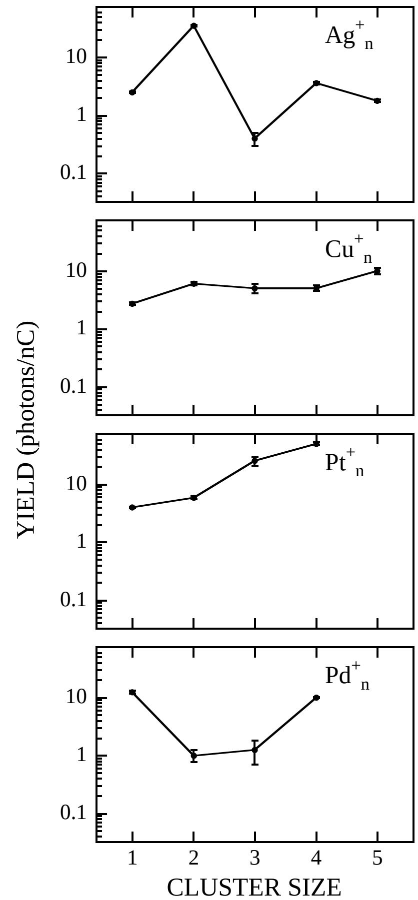

Fig. 3. Total photon yields *versus* cluster size for Ag_n^+, Cu_n^+, Pt_n^+ and Pd_n^+ ($n = 1 \ldots 5$).

photon intensities. However, employing four optical filters ($\lambda = 400, 500, 600, 700$ nm, FWHM = 80 nm) the emission intensity variation with wavelength was approximately determined. To suppress the photon background due to light emission from the cluster source, the beam is deflected by 90° and a light trap is installed. The ion-optical components are coated with carbon. This configuration largely enhances the signal-to-noise ratio.

3 Results and discussion

For each cluster size the photon intensity is measured as a function of cluster ion beam current to determine the photon yield (counts per incident charge). The cluster current is measured with a Faraday cup at the very end of the vacuum chamber to avoid an influence on the beam geometry. Owing to their high current intensities Ag_1^+ and Ag_2^+ clusters serve as convenient probes for the present investigations. The photon intensity for Ag_2^+ in Figure 2 shows a linear relationship with the cluster current, implying that the emission process involves single clusters. Figure 3 shows a compilation of the photon yields measured for Ag_n^+, Cu_n^+, Pt_n^+ and Pd_n^+ ($n = 1 \ldots 5$) clusters. Distinct cluster size effects are readily observed. While the data from many different experimental runs show identical relative yields the absolute photon intensities exhibit some variability. Most notably, the emission is minimal for dimers of Pt and Pd whereas Ag exhibits a dominant maximum for this cluster size. The odd-even effect observed for the small silver cluster ions possibly reflects their underlying electronic structure [23].

Figure 4 displays the total photon yield for Ag_2^+ dimers *versus* the total pressure when He is introduced in the chamber. The linear photon yield behaviour is probably due to an increased deexcitation induced by cluster-gas particle collisions [24,25]. By extrapolating these values to zero pressure, a residual photon yield remains, indicating that the observed photon emission cannot be explained only with collisions between clusters and residual gas particles. Figure 5 displays in a semilogarithmic plot the total photon yield for Ag_2^+ dimers *versus* the total pressure for two non-reactive gases (He, N_2). In the high pressure range ($p > 10^{-6}$ Torr), the intrinsic emission from clusters may be covered by emission from gas particle deexcitations [24]. At low pressures ($p < 10^{-6}$ Torr), one finds again a residual contribution which does not vary with pressure. Therefore we attribute our

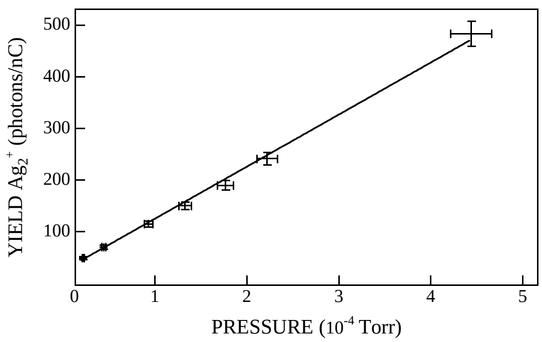

Fig. 4. Total photon yield observed for Ag_2^+ *versus* total pressure when He is introduced in the chamber. The linear dependence indicates a collision induced deexcitaion of the excited Rydberg states (see text).

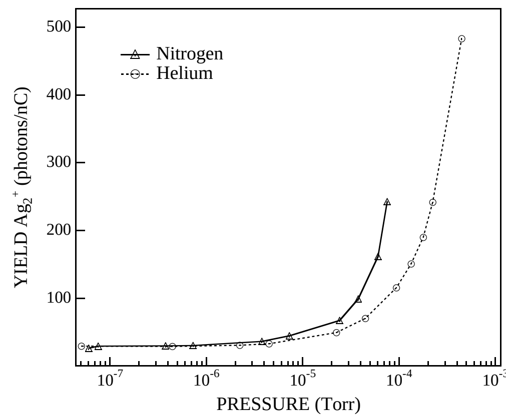

Fig. 5. Photon yield observed for Ag_2^+ *versus* pressure for two non-reactive gases: He, N_2. We note the semi-logarithmic presentation of these data. It clearly shows the constant photon yield at pressures lower than 10^{-6} Torr. For He, the same data set as in Figure 4 was used.

observations measured at 1.5×10^{-8} Torr to spontaneous emission from the clusters themselves.

Spectrally resolved measurements made with optical filters for Ag_1^+ and Ag_2^+ and normalized by the quantum efficiencies of the detection setup show a monotonous increase of the emission yield from 400 nm to 800 nm for both cluster sizes. Therefore, the measured higher photon yield for Ag_2^+ in comparison to Ag_1^+ is not caused by the wavelength dependent sensitivity of the photomultiplier.

For the small cluster sizes studied here ($n = 1 \ldots 5$), the black-body model [16–19] based on the emissivity of spherical particles containing several hundred atoms is not applicable. Compared to chemiluminescence [21], processes with much longer lifetimes are involved in our experiments. In the present type of sputter-source [8–14] where Xe ions of 30 keV kinetic energy impinge on the target, doubly-charged clusters have been detected after a flight time of ≈ 0.1 ms [14]. Therefore highly excited Rydberg states lying just below the ionization continuum of the single ionized cluster can also be populated. But in our experiment, electrical fields up to 1 kVcm^{-1} would ionize these states [26–28]. Thus no radiative deexcitations from these high lying Rydberg states would be observed. We propose that in our experiment, photon emission occurs by means of radiative electron deexcitation of metastable excited states which are populated during the high-energy sputtering process. Decay of these states *via* spin forbidden transitions exhibit long lifetimes [29–33]. Interaction of clusters with gas particles can fasten the decay process, which would lead to higher photon intensities as shown in Figures 4 and 5. In principle, spectrally resolved observations would permit to distinguish between emission from the cluster itself and emission enhanced by cluster-gas collisions. Such measurements would lead to a better insight into the physical origin of the photon emission process.

4 Summary

In summary, we report on observation of photon emission from free ionized mass-selected clusters produced with a sputter cluster source. The photon intensities are shown to quantitatively depend on the cluster sizes and their chemical identity. In the low pressure range (p $< 10^{-6}$ Torr), the observed photon emission is independent of the residual gas pressure and is therefore attributed to the clusters themselves. The observations are interpreted in terms of emission from ionized atoms and clusters which relax from metastable excited states *via* spin forbidden transitions.

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