

# Optical spectroscopy on size selected gold clusters deposited in rare gas matrices

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**Abstract.** We report on the successful “soft-landing” of size selected Au trimers in solid Krypton matrices. The Au cations are produced by sputtering, mass-selected in a quadrupole mass spectrometer, co-deposited with Krypton on a cooled CaF<sub>2</sub> substrate, and neutralized by low energy electrons. The deposition of low kinetic energy cations (10 eV) gives rise to strong excitation bands, detected by the emitted fluorescence light, which are unambiguously attributed to Au trimers. The deposition and fragmentation process is qualitatively discussed.

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## 1. Introduction

The spectroscopic techniques, so useful in molecular and solid state physics, have only recently been applied with some success to metal clusters. Information about cluster excited states have been obtained from photoelectron studies [1] and photodepletion spectra [2]. However well resolved gas phase spectra have only been obtained for dimers and a small number of trimers, i.e. Cu, Na, Al, Ni, Ag, and Li. The majority of spectroscopic measurements have employed matrix isolation techniques [3], which have the advantage that large numbers of clusters can be accumulated in the matrix and measured at controlled temperature by absorption, fluorescence, Raman, ESR, etc. techniques. However the matrix samples are usually obtained by simultaneous condensation of atomic vapor and rare gas atoms, and cluster formation depends upon the deposition conditions and the aggregation process. As a consequence matrix samples contain an unknown distribution of cluster sizes, and the interpretation of measurements is hampered by ambiguities in assigning the spectral features to a given size cluster.

The assignment problem can be solved by preparing matrices which contain single sized clusters. One way is to prepare cluster ions in a beam, to mass select them and to

neutralize them during deposition, in order to prevent charging of the matrix. Such an approach requires an intense source of cluster ions (typically several nA mass-selected), an effective means for collecting and neutralizing the ions, and that the clusters be decelerated before being frozen into the matrix (*soft-landed*) in order to avoid fragmentation. In this paper we present, as an example of the possibilities of this new preparation technique, recent results on the successful *soft-landing* and the fluorescence spectroscopy of Au trimers. A detailed account of the *soft-landing* and spectroscopy of Ag dimers and trimers is given elsewhere [4].

## 2. Experimental

The cluster deposition source has been described in detail in [4]. Briefly Au cluster ions are sputtered from a metal target using an intense, high energy (typically 10 mA, 20 keV) Krypton ion beam. The cluster cations are extracted at 90° to the primary beam, focused into a *Bessel Box* type energy filter and mass selected by a quadrupole mass filter. Cluster ions are decelerated before deposition to typically 10 to 20 eV and then codeposited with the matrix gas on a cold (10 K) CaF<sub>2</sub> window cooled by a closed cycle refrigerator. The deposition window is largely enclosed in a conducting cage, which serves to decelerate the cluster ions, whose deposition energy is adjusted by changing the potential difference applied between the Au sputtering target and the cage. Typical measured currents for Au cations are: Au<sup>+</sup> (65 nA), Au<sub>2</sub><sup>+</sup> (25 nA), Au<sub>3</sub><sup>+</sup> (8 nA), Au<sub>4</sub><sup>+</sup> (nA), and Au<sub>5</sub><sup>+</sup> (5 nA) at 100 eV kinetic energy. However usable fluxes were obtained even at deposition energies as low as 2 eV. The ions were neutralized by a charge cloud of electrons maintained in the proximity of the CaF<sub>2</sub> window. Since metal cluster ionization potentials are large compared to the cluster bond energies, we suppose that in a successful *soft-landing* the neutralization step takes place on, or very near to, the matrix surface.

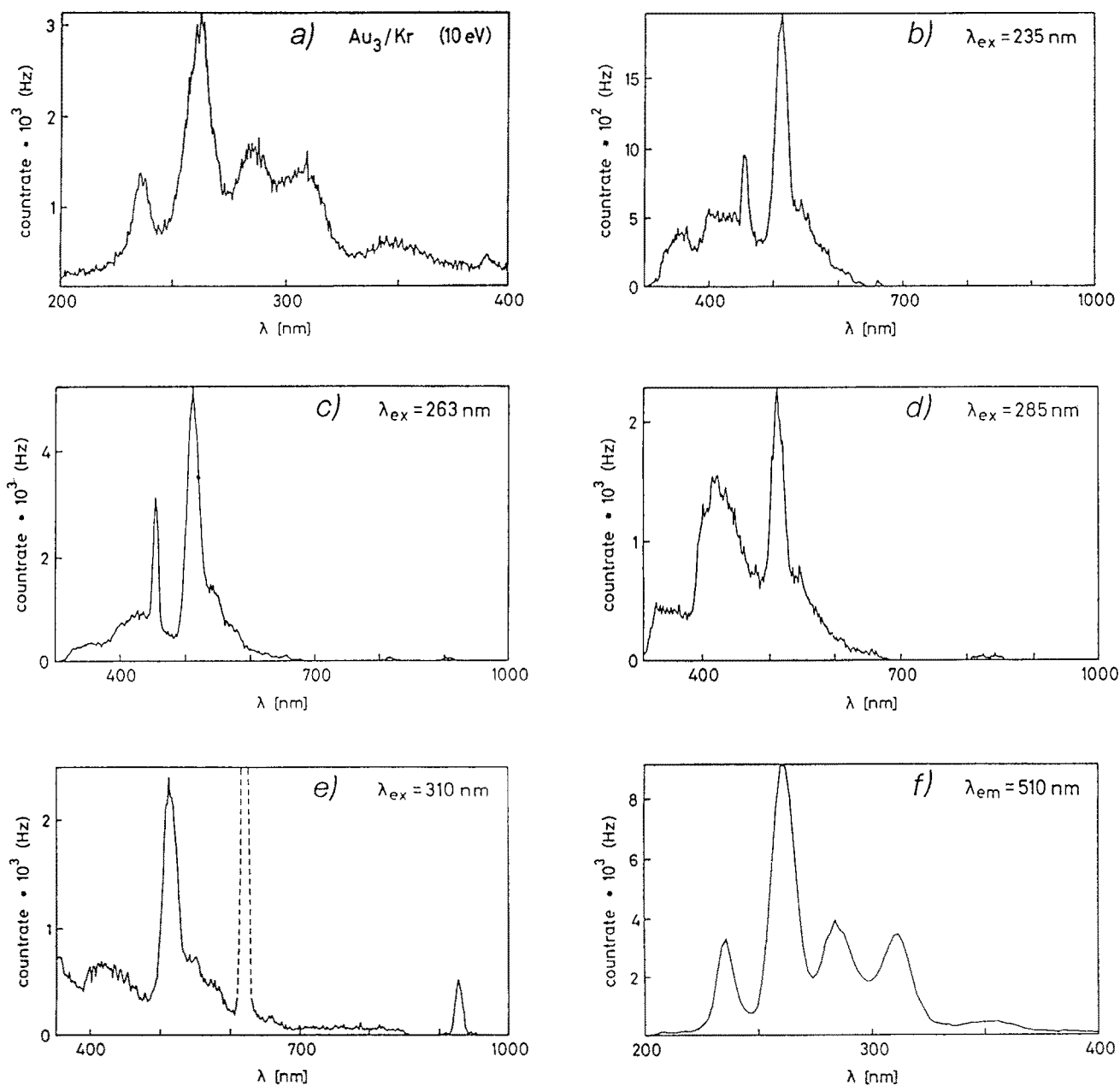
Matrix samples were studied in situ using both excitation and fluorescence spectroscopy. The light from either a

deuterium or tungsten/halogen lamp was dispersed by a monochromator (mono I) and focused onto the sample. The emitted light was collected at  $90^\circ$ , filtered (in most instances) by a long pass filter (LPF), focused into a second monochromator (mono II), and then detected. The emission spectra are analyzed in three different ways. In the first method, mono II is operated in zeroth order and the excitation spectra are recorded by scanning mono I. The scattered light is efficiently eliminated by the use of long pass filter, without blocking the matrix emission spectra, which are heavily red shifted [5]. In the second method resolved fluorescence spectra are obtained by

scanning mono II whilst exciting at a fixed wavelength transition found by method I. We have often found that certain electronic transitions emit in characteristic wave length regions. In these cases, as will be demonstrated for  $Au_3$ , it is useful to operate mono II as a band pass filter whilst recording excitation spectra by scanning mono I.

### 3. Results and discussion

We show in Fig. 1 several spectra of Au trimers deposited during 34 min with a cluster ion current of 4.2 nA, which



**Fig. 1.** Spectra of an unannealed Kr matrix ( $CaF_2$  substrate) following the deposition of gold trimers at 10 eV. **a** shows a total excitation spectrum using a 418 nm LPF. **b–e** give resolved fluorescence spectra obtained by exciting at, respectively, 235, 263, 285 and 310 nm. **f** pertain to excitation spectrum obtained by detecting light emitted at 510 nm

corresponds to about  $5 \cdot 10^{13}$  impinging trimers. The average kinetic energy of the incoming ions was equal to 10 eV, and the Kr to metal ratio  $10^5:1$  to prevent any aggregation of the deposited clusters. The spectra have been recorded using a deuterium lamp. The results of more extensive measurements using a tungsten/halogen lamp in order to increase the scanning range are reported in Table 1. Prior to these measurements, similar experiments were carefully done with Au atoms and dimers, the corresponding absorption and emission bands are given in Table 1. Figure 1a shows the excitation spectrum using method I (scanning mono I while mono II was set at 0 nm) and a LPF of 418 nm. Five absorption bands centered at 235, 263, 285, 310 and  $\sim 345$  nm are clearly distinguishable. Two of them (235, 263) are located at the position of atomic absorption lines (Table I), which are however narrower than the observed peaks. In order to sort out specific features that can be attributed to  $\text{Au}_3$ , we have used method II, i.e. the excitation light is set on a transition and mono II is scanned. This leads to the fluorescence spectra shown in Fig. 1b to e. There are essentially two emission regions centered at  $\sim 453$  nm and 510 nm. The two narrow peaks at 620 nm and 930 nm in Fig. 1d are due to reflections of second and third order of mono I. The emission at 453 nm comes from atoms, which clearly shows that there is some fragmentation in our sample, whilst the emission at 510 nm is only present when trimers are deposited (Table 1). In order to obtain a *pure* trimer spectrum, we thus set mono II at 510 nm and scanned mono I, the result is given in Fig. 1f. Table 1 summarizes the absorption bands attributed to trimers, as well as the corresponding emission bands. Although the positions of absorption bands in matrices are displaced with respect to the gas phase, these shifts are generally less than 5% [5]. A more thorough discussion of these data

**Table 1.** Summary of absorption and emission bands found for gold atoms, dimers and trimers in krypton matrices. Underlined transitions denote a dominant or characteristic emission. Units are nm

Species	Absorption bands	Corresponding emission bands	
Au	233 <sup>a</sup>	453	816
	261	453	816
Au <sub>2</sub>	215 <sup>a</sup>	280	750
	251 <sup>a</sup>	665	810
	<u>299</u>	<u>665</u>	<u>810</u>
	<u>347</u>	<u>665</u>	<u>810</u>
Au <sub>3</sub>	233	<u>510</u>	
	<u>258</u>	<u>510</u>	
	281	<u>510</u>	
	308 <sup>a</sup>	<u>510</u>	
	388	580	660
	458	580	820

<sup>a</sup> The 233, 215, 251 and 308 nm bands are averages of doublet peaks at (232, 235), (212, 217), (249, 253) and (305, 311) nm, respectively

and comparison with published measurements is deferred to a later article.

The presence of atomic features in Fig. 1 implies that some trimers were fragmented, the same is true for dimers. Fragmentation appears to be a complex phenomenon involving gas-phase collisions in addition to the neutralization and landing steps. In the case of  $\text{Ag}_2$  [4] we have found that when deposited at low energies ( $< 10$  eV) the fragmentation rate (F) is about 40%, it minimizes around 20 eV ( $F = 25\%$ ) and then increases continuously up to  $F = 80\%$  at 100 eV. Such an analysis is difficult and it has not yet been carefully done for Au dimers and trimers. However Fig. 1 clearly shows that the fragmentation rate for  $\text{Au}_3^+$  is low (compare e.g. Fig. 1a and Fig. 1f). Notice also that the term *soft-landing* is misleading in the context of a 10–20 eV dimer or trimer (cohesive energy per atom  $\sim 1$  eV) impinging on a Kr matrix whose cohesive energy is approximately 100 meV/atom. Under our experimental conditions, a cluster will dissipate its kinetic energy to the rare gas solid long before it interacts with any subsequent incoming (i.e. metal or Kr) particle. The deposition process can thus be considered as a form of low energy sputtering, we estimate [4, 6] that one rare gas atom should be ejected for each impinging particle. This process will also induce the displacement of a large number of matrix particles, since the kinetic energy of the incoming cluster is about 100 times larger than the rare gas binding energy. Under these conditions the *soft-landing* corresponds probably to a series of soft collisions which efficiently transfer the kinetic energy to the matrix. We do not, at present, have a good model to predict the fragmentation ratio.

In summary, we have shown in the particular case of  $\text{Au}_3^+$  that size selected cluster ions can be neutralized and *soft-landed* in a rare gas matrix. We have obtained good quality fluorescence spectra and unambiguously identified several absorption bands in  $\text{Au}_2$  and  $\text{Au}_3$  deposited in a Kr matrix. A better understanding of the deposition process needs more carefully controlled experiments which are in progress.

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