

High resolution photodetachment spectroscopy of jet-cooled metal cluster anions: Au_2^- and Ag_3^-

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In recent years an increasing amount of theoretical and experimental data regarding the electronic structure of metal clusters have become available.¹ In addition, there are predictions of the geometrical structure,² but only a few experimental approaches really determine these geometries.³ Vibrational spectroscopy of gas phase metal clusters is a potential source of structural information, especially if enough modes are observed for a complete analysis. Experimental methods like laser fluorescence spectroscopy⁴ or resonantly enhanced multiphoton ionization,⁵ which obtain sufficient resolution for vibrational analysis, are mostly restricted to very small clusters such as dimers and trimers.⁶

Photodetachment spectroscopy with fixed frequency lasers allows the examination of anionic and neutral ground states and the excited states of the neutral cluster.⁷ C. W. Lineberger's group has recently determined the vibrational frequencies and parameters of the potential curves of ground states of the neutral and negative charged Au dimer.⁸ The use of a hemispherical analyzer limited the resolution to 6–9 meV and the anion temperature of about 350 K caused the appearance of several "hot bands," which further complicated the analysis.

To obtain higher resolution and lower temperatures we combined a laser vaporization source, producing jet-cooled anions, with a zero electron kinetic energy spectrometer⁹ (ZEKES) (Fig. 1). This method has the advantage of high resolution^{9,10} since only electrons of low kinetic energy are detected. The cluster source is described in detail elsewhere.¹¹ The mixture of neutral, negative, and positive

charged metal clusters is flushed through a 4 cm long extender (diameter 2 mm) and a conical nozzle (15° opening angle, length 3 cm) into vacuum. After passing the skimmer, the anions are accelerated to ~ 20 km/s by a pulsed electrical field arrangement according to Wiley–McLaren¹² resulting in the separation of the different sized clusters. The anion beam is focused into the interaction area of the ZEKES. Electrons from a selected bunch of anions are detached by a frequency calibrated¹³ pulsed tunable laser. The interaction area is carefully shielded against external magnetic and electric fields. After ~ 300 ns electrons with higher kinetic energies (> 2 meV) have left the interaction region and now an extraction voltage (1 V) is applied to the upper electrode. A spectrum is obtained by recording the electron intensity while tuning the laser wavelength. We achieved a FWHM of individual vibrational lines of 1.5 meV (Fig. 2).

Our first results studying Au_2^- are displayed in Fig. 2. The transitions are easily assigned: There is a change in the vibrational spacings from roughly 190 cm^{-1} to 150 cm^{-1} at ~ 1.93 eV, indicating the difference between transitions from the ground state of Au_2^- to excited vibrational levels of Au_2 and transitions from excited states of the anion to the ground and excited states of the neutral, respectively. In addition, the relative intensities of the $0-v''$ ($v'' = 1,2,3$) lines vary, depending on the expansion conditions (i.e., temperature), while the $v'-0$ ($v' = 0,1,2,3$) have a constant intensity distribution. The spacings and intensities are listed in Table I.

Note the strong increase of the electron intensity at the

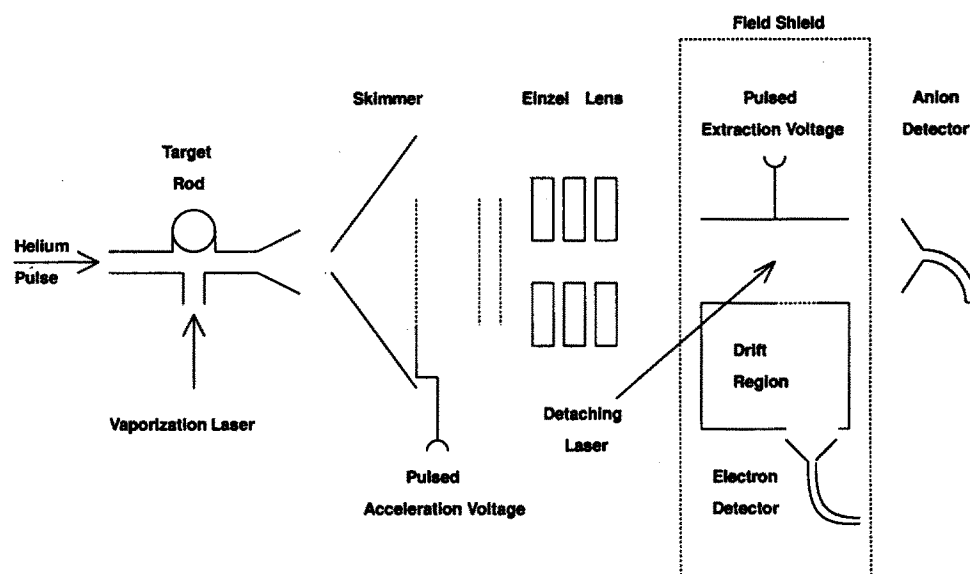


FIG. 1. Experimental setup.

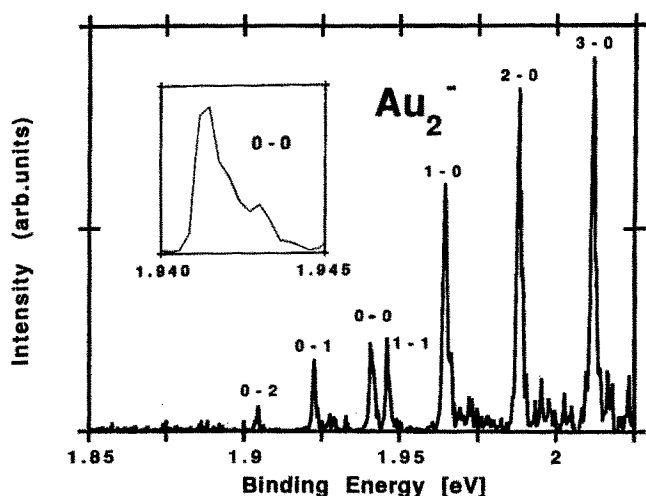


FIG. 2. A typical ZEKE spectrum of Au_2^- . The binding energy equals the photon energy of the detaching laser. The insertion shows a high resolution spectrum of the 0-0 transition. The FWHM is about 1.5 meV. The asymmetric line shape is typical for this type of spectroscopy (Ref. 10).

threshold of each vibrational transition. This is predicted by Wigner¹⁴ for a transition from a p -like molecular orbital to a s -like free electron wave. The onset energy of a transition is determined by linear extrapolation of the signal on the low energy side. The adiabatic electron affinity (the position of the 0-0 transition) of $1.940 \text{ eV} \pm 0.5 \text{ meV}$ is in good agreement with C. W. Lineberger's recent result.⁸ The error limit of $\pm 0.5 \text{ meV}$ includes rotational effects, the resolution of the laser and the uncertainty in the determination of the onset.

The vibrational frequencies for Au_2^- and Au_2 (see Table I) are very similar to the data of Ref. 8. The measured relative intensities of single lines are strongly dependent on the photon flux due to space charging effects. Thus, the values listed in Table I are taken at a low laser fluence ($\sim 10 \mu\text{J}/\text{cm}^2$). The intensities of the $\nu'-0$ transitions are direct measures of the Frank-Condon (FC) factors for these transitions. These intensities agree with those calculated in Ref. 8. Using the FC factors in Ref. 8 for the 1-1 and 0-1 transitions we estimated a vibrational temperature of $165 \pm 30 \text{ K}$ (compared to 350 K from Ref. 8). This relatively low temperature is achieved by careful optimization of experimental conditions.

For Ag_3^- we find a single symmetric peak centered near 2.452 eV within the energy range of 2.35 to 2.5 eV. The FWHM of this peak is less than 10 meV, which is about 4 times smaller than that reported in Ref. 8. The onset of the electron signal is about 2.44 eV. By adjusting the source parameters to result in less effective cooling, the line shape becomes slightly asymmetric and the onset shifts towards lower energies. Thus, the differences between our results and Ref. 8 may be due to temperature effects. The occurrence of only a single feature is consistent with the assumption that the transition is from the linear Ag_3^- to the linear state of Ag_3 , $\sim 0.05 \text{ eV}$ above the triangular ground state.¹⁵

These first encouraging results show the importance of temperature effects in photoelectron spectra of metal clus-

TABLE I. Positions of the lines shown in Fig. 2. The positions are determined by the intersection of a straight line, fitted to the low energy slope of the peak, with the zero line. The relative intensities are averaged values of several spectra taken at a laser fluence of ($\sim 100 \mu\text{J}/\text{cm}^2$). The error is mainly due to intensity fluctuations of the cluster source. The estimated vibrational temperature is $165 \pm 30 \text{ K}$.

Assignment $\nu'-\nu''$	Position (cm^{-1})	Spacing (cm^{-1})	Intensity $\pm 20\%$
3-0	16207 ± 4	190	5.5
2-0	16017	186	4.7
1-0	15831	145	3.8
1-1	15686	44	1.1
0-0	15642	147	1
0-1	15495	146	0.85
0-2	15348	147	0.21
0-3	15201		0.01

ters. We plan to apply high-resolution electron spectroscopy to study more complex systems such as larger clusters of metals and carbon.

We wish to thank C. W. Lineberger and his co-workers for sending us the preprint (Ref. 8) of their recent work on the coinage metal clusters. In addition, we thank S. Dougal and P. Rabinowitz for experimental support and advice regarding the laser system.

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