High resolution photoelectron imaging of Au2
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High resolution photoelectron imaging of Au$_2^-$

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We report high resolution photoelectron spectra of Au$_2^-$ using a newly built photoelectron imaging apparatus. Vibrationally resolved photoelectron images are obtained for the ground state detachment transition of Au$_2^-$ at various photon energies (442.80–670.18 nm) at a resolution of 3 cm$^{-1}$ for low energy electrons. Franck-Condon simulations yield the vibrational temperature of Au$_2^-$ and the high resolution data yield accurate spectroscopic constants for the ground states of Au$_2$ and Au$_3^-$. The electron affinity of Au$_2$ is measured to be 1.9393 ± 0.0006 eV. A more precise value for the Au$_2^-$ dissociation energy is also obtained as 1.937 ± 0.005 eV. © 2013 AIP Publishing LLC.

Anion photoelectron spectroscopy (PES) has proven to be a powerful technique for the study of size-selected atomic clusters. It probes directly the electronic and, in some cases, vibrational structures of the corresponding neutral species. However, the resolution of PES is limited to a few meV in the best cases, which is not sufficient to resolve low frequency vibrations. Zero electron-kinetic-energy (ZEKE) spectroscopy can reach much higher resolution of a few cm$^{-1}$ or even sub-wavenumbers. But its application to anions has been limited because of the threshold law, which favors detachment of $p$-like electrons with $s$ outgoing. Photoelectron imaging allows very low energy electrons to be detected, providing a much higher resolution method for PES. The imaging technique was originally developed to record spatial distributions of photodissociation products, but was soon applied to photoelectrons from multiphoton ionization of Xe and size-selected cluster anions. With the development of the velocity map imaging (VMI) technique by Eppink and Parker, photoelectron imaging has evolved into a powerful alternative PES method over the past decade. The advantage of photoelectron imaging lies at its high detection efficiency while yielding photoelectron angular information at the same time. The sensitivity of the imaging method to slow-electrons has allowed high-resolution photoelectron spectra to be obtained for near zero-eV electrons. The latter is known as SEVI by the Neumark group for slow electron velocity-map imaging. More recently, rotational resolution has been reported for slow electron imaging of small neutral molecules using multiphoton ionization.

We designed previously a photoelectron imaging system to study the angular distributions of multiply charged ions from an electrospray ionization source. Recently, we have developed a high resolution photoelectron imaging system for the study of size-selected cluster anions produced from a laser vaporization supersonic cluster source. In the current work, we present our first result on Au$_2^-$ as a test case reporting a more accurate value of the electron affinity (EA) and more accurate spectroscopic constants for the anion. Au$_2^-$ was selected because of its well-known spectroscopy. In particular, a vibrationally resolved PES spectrum of Au$_2^-$ was first reported by Lineberger and co-workers using a hemispherical electron analyzer at a resolution of ~6 meV and a vibrational temperature of 350 ± 25 K. Gantefor and co-workers reported a ZEKE spectrum of Au$_2^-$ in the photon energy range of 1.85 to 2.025 eV at a spectral resolution of 1.5 meV and a vibrational temperature of 165 ± 30 K. In the current work, we report photoelectron images of Au$_2^-$ in the photon energy range of 1.8470 eV (671.28 nm) to 2.8000 eV (442.80 nm) at a vibrational temperature of 175 ± 25 K and a kinetic energy resolution of 2.8 cm$^{-1}$ for slow electrons.

Details of the new apparatus will be published separately. Briefly, the laser vaporization supersonic cluster source and the time-of-flight mass spectrometer are similar to our magnetic-bottle apparatus, which were described in detail before. A gold disk was used as the laser vaporization target with a helium carrier gas seeded with 5% argon, which produces relatively cold gold cluster anions. Clusters formed inside the nozzle were entrained by the carrier gas and underwent a supersonic expansion. After a skimmer, anions from the collimated cluster beam were extracted perpendicularly into a time-of-flight mass spectrometer. The Au$_2^-$ dimer of current interest was mass-selected and focused into the collinear VMI system. The VMI lens is based on the design by Suits and co-workers for ion imaging, which is modified and optimized for photoelectron imaging. Photoelectrons are accelerated toward a position-sensitive detector with a 75 mm diameter micro-channel plate coupled to a phosphor screen and a charge-coupled device (CCD) camera. A National Instrument PXI-mainframe system is used to control the whole apparatus and for data acquisition. The tunable detachment radiation (222–709 nm, linewidth <0.3 cm$^{-1}$) is from a Continuum Sunlite OPO system pumped by an injection-seeded Continuum Powerlite laser. A half-wave plate combined with a high-quality Glan-Laser polarizer is used to achieve a high degree of polarization parallel to the imaging detector plane. For the current work, photoelectron images were averaged with 50 000 to 200 000 laser shots and quadrant-symmetrized before inverse-Abel transformation to obtain the three-dimensional (3D) electron imaging data. The vibrational temperature of Au$_2^-$ was 25 K and a vibrational temperature of 350 ± 25 K. Gantefor and co-workers reported a ZEKE spectrum of Au$_2^-$ in the photon energy range of 1.85 to 2.025 eV at a spectral resolution of 1.5 meV and a vibrational temperature of 165 ± 30 K. In the current work, we report photoelectron images of Au$_2^-$ in the photon energy range of 1.8470 eV (671.28 nm) to 2.8000 eV (442.80 nm) at a vibrational temperature of 175 ± 25 K and a kinetic energy resolution of 2.8 cm$^{-1}$ for slow electrons.© 2013 AIP Publishing LLC.

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FIG. 1. Photoelectron images of \( \text{Au}^{2-} \) taken at a photodetachment wavelength of 590.41 nm (2.1000 eV). (a) The raw image. (b) The 3D view of the raw image after inverse-Abel transformation. (c) The 2D view of the inverted image overlaid with the electron kinetic energy distribution obtained by integrating the electron counts circumferentially.

Figure 1 illustrates the reconstruction process of photoelectron images and the conversion from images to electron kinetic energies (\( \text{KE} \propto r^2 \), where \( r \) is the radius of the image). The image in Fig. 1 corresponds to detachment transitions from the ground electronic state of \( \text{Au}^{2-} (\tilde{2}\Sigma_u^-) \) to that of \( \text{Au}_2 (\tilde{1}\Sigma_g^+) \) at a photon energy of 2.1000 eV (590.41 nm). Figure 1(a) shows the raw image, where the circles represent electrons with different kinetic energies or transitions to different vibrational levels of \( \text{Au}_2 \) in its ground electronic state. Figure 1(b) displays the 3D view of the image after the inverse-Abel transformation, while Fig. 1(c) is the 2D projection overlaid by the electron kinetic energy distributions obtained by integrating all electron counts circumferentially. The electron binding energy spectra presented in Figs. 2–4 are obtained by subtracting the electron kinetic energy spectra from the respective detachment photon energies. The photoelectron images shown in Fig. 1 are fairly isotropic, which are also the cases for all the images at lower photon energies (Fig. 4).

We showed previously that supersonic cooling was critical to obtain well-resolved photoelectron spectra by our magnetic-bottle apparatus for clusters produced from a laser vaporization source. We found that the resident time of the cluster inside the nozzle was important to achieve better cooling, but we were not able to estimate the vibrational temperatures quantitatively. The vibrational resolution in the new imaging apparatus afforded us an opportunity to study the vibrational cooling for \( \text{Au}^{2-} \). Figure 2 displays the spectrum of \( \text{Au}^{2-} \) at 442.80 nm (2.8000 eV) under the coldest conditions achievable for this cluster, in comparison with the Franck-Condon simulation using the Pescal program. Because the resolution of SEVI depends on the electron kinetic energies, we fit the data in the electron velocity space and then converted both the experimental spectra and the simulation to the electron binding energy scale. The 442.80 nm
The electron affinity (EA) of Au$_2$ was determined as $1.9393 \pm 0.0006$ eV from the $0 \leftarrow 0$ transition (peak $h$ in Figs. 3 and 4). This value was measured from the low photon energy spectra at 635.82 nm (Fig. 4(c)) and 619.92 nm (Fig. 4(d)). The current result represents the most accurate EA value for Au$_2$, as compared with the two previous measurements in Table I. The peaks observed in the spectra at 652.55 nm (Fig. 4(b)) and 671.28 nm (Fig. 4(a)) are entirely due to vibrational hot bands of Au$_2^-$. The lowest binding energy peak observed ($a'$ in Fig. 4(a)) corresponds to $0 \leftarrow 6'$ (Table S1). We estimated a population of $\sim0.1\%$ for the $v'=6$ vibrational level of Au$_2^-$ at $T_{\text{vib}} \sim 200$ K. That this transition was observed at all indicates the sensitivity of the imaging technique. The observation of this weakly populated vibrational hot band was also benefited from the fact that there was no background noise at this low photon energy. The spectra shown in Figs. 3 and 4 also reveal a threshold enhancement phenomenon for the peaks on the very high binding energy side at each photon energy. For example, the peak labeled as $y$ in Fig. 3, corresponding to the $7 \leftarrow 1'$ transition, is much more intense than the calculated Franck-Condon factor (Fig. 2). A long-lived excited state was observed previously for Au$_2^-$, with an excitation energy slightly above the detachment threshold. Autodetachment can happen via this excited state, giving rise to the anomalous intensities near threshold. A similar argument has been invoked previously to explain anomalous vibrational intensities in photoelectron imaging of C$_4$H$^-$. In addition, the Wigner threshold law favors near threshold detachments with $s$-outgoing waves, which has been observed in SEVI previously.
We fitted the observed vibrational spacings for both the anionic and neutral ground state of Au$_2$ to an anharmonic oscillator described by the Morse potential and obtained a relatively accurate harmonic vibrational frequency and anharmonicity for Au$_2^-$, as given in Table I along with literature values. Furthermore, using the accurate EA value measured in this work together with a redefinition of the dissociation energy for Au$_2$ by Morse and co-workers, we obtained a more accurate dissociation energy for the ground state of Au$_2^-$ as 1.937 ± 0.005 eV (Table I).

In conclusion, we report high resolution photoelectron spectra of Au$_2^-$ using a newly built photoelectron imaging instrument. Accurate spectroscopic constants are obtained for the ground electronic state of Au$_2^-$, as well as a more accurate electron affinity for Au$_2$. Even with a relatively cold cluster beam, photodetachment transitions from $v' = 6$ from Au$_2^-$ were observed due to the high sensitivity.
of the imaging method. The high resolution capability of the imaging method should allow accurate vibrational and electronic information to be obtained for a broad range of size-selected atomic clusters.

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\[ \text{TABLE I. The obtained spectroscopic constants for } \text{Au}_2 \text{ and } \text{Au}_2^- \text{, in comparison with those from the literature.} \]

<table>
<thead>
<tr>
<th>\multicolumn{1}{c}{\text{Current work}}</th>
<th>\multicolumn{1}{c}{\text{Literature}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{EA (eV)}</td>
<td>\text{1.9393 ± 0.0006}</td>
</tr>
<tr>
<td>\text{$\omega_x$ (cm$^{-1}$)}</td>
<td>\text{194 ± 9}</td>
</tr>
<tr>
<td>\text{$\omega_x\chi_x$ (cm$^{-1}$)}</td>
<td>\text{[0.41]$^d$}</td>
</tr>
<tr>
<td>\text{D$_0$ (eV)}</td>
<td>\text{2.290 ± 0.008$^c$}</td>
</tr>
<tr>
<td>\text{$r_v$ (Å)}</td>
<td>\text{2.4715$^g$}</td>
</tr>
</tbody>
</table>

|$^a$From Ref. 28.  
|$^b$From Ref. 7.  
|$^c$From Ref. 31.  
|$^d$The values in brackets are estimates from this work.  
|$^e$From Ref. 30.  
|$^f$Calculated by the relationship: \( D_0 (\text{Au}_2^-) = D_0 (\text{Au}_2) + \text{EA (Au)} - \text{EA (Au)} \). The \( D_0 (\text{Au}_2) \) value is from Ref. 31, the \( \text{EA (Au)} \) value is from the current work, and the \( \text{EA (Au)} \) is from Ref. 45.  
|$^g$From Ref. 29.