

Vibrational spectroscopy of clusters using a "magnetic bottle" electron spectrometer

H. Handschuh, G. Ganteför, and W. Eberhardt
Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

The design of a high resolution "magnetic-bottle"-type time-of-flight electron spectrometer suitable for the study of mass-separated metal and semiconductor cluster anions is described. A high collection efficiency is achieved by using magnetic fields to guide the photoelectrons, so that vibrationally resolved photoelectron spectra can be recorded at a low laser pulse energy ($<10 \mu\text{J}$ focused to 1 mm^2) avoiding multiphoton processes. Spectra of clusters with a very low relative abundance, for example the products of chemical reactions involving clusters, can be recorded and an energy resolution of 6 meV (48 cm^{-1}) achieved.

I. INTRODUCTION

The determination of the geometric structure of nanoparticles (clusters) is a difficult experimental task and very few techniques can provide significant data suitable for a comparison with theoretical predictions.¹ Established structural analysis techniques such as x-ray diffraction or nuclear magnetic resonance cannot be used because it is not possible to generate sufficient amounts of particles of a certain size.

The geometric structure of molecules and clusters in the gas phase can be studied by vibrational spectroscopy. However, in the case of clusters established techniques like resonant two photon ionization cannot be applied because of the problem of mass separation and the short lifetimes of the excited electronic states of the clusters.^{2,3} Recently, photoelectron spectroscopy of anions⁴⁻¹² (PESa) was used successfully to study the electronic structure of clusters. Because the target is a negatively charged particle beam the size of the clusters can be selected accurately by mass spectroscopy methods prior to the detachment process. In addition, photoelectron spectra deliver information about the final states, which are the ground and excited states of the neutral clusters, and the spectra can be directly compared with calculations on neutral clusters.¹³⁻¹⁵

There are several experimental problems involved with PESa: First, it is difficult to achieve an energy resolution sufficient to resolve the vibrational modes of metal and semiconductor clusters. Only in relatively few cases have vibrationally resolved PESa spectra been obtained for such clusters.^{4,8-10} The overall resolution is limited by the energy resolution of the electron spectrometer [hemispherical analyzer,^{4,7} time-of-flight (TOF) electron spectrometer,^{5,6,8,11,12} zero kinetic energy electron spectrometer],⁸⁻¹⁰ the vibrational and rotational broadening caused by the internal temperature of the particle ("hot bands"), and the overlap of several modes excited by the detachment process ("cold bands").

A problem concerning the study of the electronic structure is the limited photon energy due to the use of lasers, since the low target density of the anion beam rules out the use of conventional light sources (He lamp, synchrotron radiation). Laser radiation used in PESa experiments can be generated by commercial cw lasers up to $h\nu=3.5 \text{ eV}$ (Ref. 4)

and by pulsed lasers up to $h\nu=7.9 \text{ eV}$ (Ref. 16) (F_2 excimer laser). In principle, higher photon energies are available using either a Raman cell¹⁷ or by frequency tripling using a gas cell,¹⁸ but the light intensity with both methods is at least 3 orders of magnitude smaller.

The "magnetic-bottle"-type TOF electron spectrometer has the advantage of a high detection efficiency for the detached electrons.^{5,11,19} Using this instrument for PESa spectra can be recorded within a few minutes or at a low photon flux (e.g., using a Raman cell) or at extremely low target densities (e.g., for the study of reacted clusters with low relative intensities).

The intrinsic energy resolution of the magnetic bottle spectrometer depends on various parameters like the length of the drift region, the length of the laser pulse, the details of the magnetic fields, and the size of the laser focus. In experiments on neutral atoms and molecules a resolution $\Delta E/E$ of about 1% is achieved.¹⁹ If applied to anions, the energy resolution of a magnetic bottle spectrometer is usually limited to about 40–300 meV (Refs. 5 and 11) so that vibrational spectroscopy is not possible. This limitation is caused by the Doppler effect due to the relatively high velocity of the anions compared with the thermal velocities of neutral targets. In the laboratory frame, the velocity of the electrons is the vector sum of the center-of-mass velocity of the emitted electrons and the velocity of the anions.^{5,11} We have designed a new type of magnetic bottle spectrometer for anion spectroscopy with an improved energy resolution of $\approx 6 \text{ meV}$. The Doppler broadening is reduced by a deceleration technique reducing the kinetic energy of the anions to less than 2.5% of the primary beam energy.

II. EXPERIMENTAL SETUP

The experimental setup suitable for photoelectron spectroscopy of cluster anions using a conventional magnetic bottle TOF electron spectrometer has been described in detail earlier.^{5,11} The cluster anions are generated by either a laser vaporization source^{20,21} or a pulsed arc cluster ion source (PACIS).^{11,22,23} After passing a skimmer the anions are accelerated in a pulsed electric field up to a kinetic energy of about 200–1000 eV. The anions separate into a chain of bunches of clusters of defined size due to their different ve-

locities, the anion beam is directed into the source region of the electron spectrometer, and a selected bunch is irradiated by a laser pulse. The detached electrons are guided by magnetic fields towards the electron detector. The kinetic energy of the photoelectrons is calculated from the measured TOF. A photoelectron spectrum is a plot of the measured electron intensity versus the binding energy, which is the difference between the photon energy and the kinetic energy.

For vibrational spectroscopy two components of the experiment are crucial: the design of the source and of the spectrometer. The following problems must be addressed.

(i) Only the ground state isomer of a cluster anion should be present in the beam. For example, for carbon clusters with more than about 10 atoms various isomers are generated by a laser vaporization source.²⁴ Since each isomer contributes to the photoelectron spectrum with different features and vibrational frequencies this mixture of isomers may yield a featureless spectrum. The amount of metastable isomers can be reduced by an annealing technique.²⁵

(ii) The cluster anions must be cooled effectively ("cold clusters"). If the vibrational temperature of the anions is too high (e.g., >350 K in the case of Au and Ag clusters) vibrational structures may be removed by the appearance of hot bands in the spectrum. For example, no vibrational structure could be resolved in the spectrum of Au₄⁻,⁴ even though the energy resolution of the hemispherical analyzer used was better than 5 meV. In contrast, a pronounced vibrational structure is found in an analogous experiment using a laser vaporization source and our improved magnetic bottle spectrometer with an energy resolution of no better than 6 meV (see below).

(iii) The energy resolution of the electron spectrometer must be sufficient to resolve the vibrational fine structure. There are several electron spectrometers currently in use for PESa, including the following.

The hemispherical analyzer.^{4,7} This dispersive spectrometer operates continuously and is suitable for experiments using continuously operating sources (afterglow discharge source, oven source). Only those electrons are detected that pass the entrance slit and have a certain kinetic energy. A spectrum is recorded by measuring the electron intensity while scanning the kinetic energy. Simultaneous detection of a range of kinetic energies is possible using a multinode or a spatially resolving detector (resistive anode and position computing electronics). Due to the limited acceptance angle only about 1% of the electrons enter the spectrometer. Due to this loss of >10⁻² an intense light source is necessary (e.g., 100 W cw laser, intracavity, Ref. 4). An energy resolution of 5–9 meV can be achieved.

*The time-of-flight spectrometer.*⁸ This spectrometer consists of a drift tube of about 1 m length. The kinetic energy of the electrons is calculated from the TOF of the electrons between the interaction region of the laser and the ion beam to the detector. Only those electrons that are emitted in the direction of the detector are detected and the energy resolution increases by increasing the length of the drift tube. However, the fraction of the detected electrons decreases correspondingly (e.g., 10⁻⁴, Ref. 8). This spectrometer is usually combined with a pulsed cluster source (laser vaporization

source) and a pulsed mass separation method (TOF mass spectrometer). The electrons are detected independent of their kinetic energy. A TOF electron spectrum is recorded by averaging the detector response for several 10⁵ cycles, and an intense UV-laser pulse serves as the light source (up to 1 J pulse energy). The energy resolution is approximately 1% of the kinetic energy of the electrons (maximum about 8 meV).

The magnetic-bottle-type time-of-flight spectrometer.^{5,6,11,12} This spectrometer is similar to the conventional TOF spectrometer, but magnetic fields are applied to direct more than 50% of the emitted electrons towards the detector. Compared with the conventional TOF spectrometer, a spectrum can be recorded with about 4 orders of magnitude lower laser intensity, a correspondingly shorter measuring time, or a correspondingly lower target density of the anion beam. However, the energy resolution decreases due to the Doppler effect. The velocity of the electrons v_e measured by the spectrometer is the vector sum of the center-of-mass velocity of the electrons $v_{c.m.}$ and the velocity of the anions v_a

$$\vec{v}_e = \vec{v}_{c.m.} + \vec{v}_a.$$

Since almost all electrons emitted in various directions with respect to the anion velocity are collected, different v_e 's are measured depending on the angle between the two velocity vectors. The maximum Doppler broadening of v_e is 2^*v_a . The resulting uncertainty of the kinetic energy of the electrons dE is (m_e =electron mass):

$$dE \sim 2m_e^*v_{c.m.}^*v_a.$$

For example, photoelectrons with a kinetic energy of 1 eV ($v_e = 590 \times 10^3$ m/s) emitted from clusters with a mass of 500 amu and a kinetic energy of 1000 eV ($v_a = 20 \times 10^3$ m/s) exhibit a Doppler broadening of 130 meV. However, the advantage of the high collection efficiency of this type of spectrometer turned out to be crucial for two reasons: (i) Spectra can be recorded at a very low laser flux (<10 μ J focused to 1 mm²). This minimizes the thermal emission signal arising from multiphoton processes and is important for the study of such clusters as large C_n⁻ clusters ($n > 10$).^{25–27} (ii) Spectra of clusters with a very low relative abundance (e.g., reactive clusters) can be recorded.²⁸

Zero electron kinetic energy (ZEKE) spectrometer.^{9,10} This spectrometer detects only electrons with kinetic energies below a certain limit, which is the energy resolution attained (typically 0.5 meV). A spectrum is recorded by measuring the intensity of the ZEKE electrons while scanning the photon energy using a dye laser. With this method spectra can be recorded with an extremely high energy resolution, providing very detailed information about the vibrational structure. However, due to the difficulties of this technique (slow electrons, stable source conditions during a scan, dye laser scans over a large spectral range, etc.) a systematic study of a considerable number of clusters of different sizes is time consuming. In addition, for several clusters thermionic emission is possible in addition to direct photoemission, even in the limit of single photon processes.²⁷ The photon is absorbed and the energy converted to heat. If the number of degrees of freedom is not too large, the hot cluster can emit

an electron after a certain delay time. This thermionic emission process yields low kinetic energy electrons with a relatively high intensity and exhibits a smooth dependence on the photon energy. Any true ZEKE signal from electronic transitions is superimposed on this intense emission signal, so that ZEKE spectroscopy might be limited to clusters that show no thermionic emission. However, thermionic emission has been found for various negatively charged clusters like W_n^- , Ni_n^- , C_n^- , Si_n^- , and Ag_n^- .²⁷

In our experimental setup we use either a laser vaporization source or a PACIS. In both sources the clusters are efficiently cooled in a He seeding gas. The clusters can subsequently be annealed in an electric discharge, and the subsequent slow cooling results in an enhanced intensity of the most stable isomers.²⁵ Our improved magnetic bottle spectrometer combines the advantages of the high resolution—comparable to the hemispherical analyzer—with the high electron collection efficiency of the standard magnetic bottle spectrometer. We now describe the design of our improved magnetic bottle electron spectrometer.

Figures 1(a) and 1(b) display a schematic view of the electron spectrometer. The bunch of anions enters the spectrometer through a metal tube (5 cm long, 4 mm i.d.). While the bunch is inside the tube its potential is switched from ground to a positive potential about equal to the kinetic energy of the anions. The tube ends 9 mm before the interaction region of the spectrometer. After passing through a gap of 5 mm the anions enter a grounded second tube (center tube) of equal size and are decelerated by the electric field between the two tubes. Depending on the exact adjustment of the potential the bunch penetrates about 3–5 mm into the grounded center tube before turning around. Because the electric field has a strong focusing effect and because the deceleration causes an additional compression of the anion bunch, the target density is maximized at the turn-around point. This deceleration technique enhances the electron signal by about an order of magnitude compared with the setup with no deceleration field.

When the bunch starts to turn around the entrance tube is switched back to ground potential. After a certain delay time the detachment laser is fired. The center tube has apertures to allow for the laser pulse to irradiate the nearly stopped bunch. Located below the turn-around point is the tip of the high-field magnet of the magnetic-bottle spectrometer. The detached electrons are guided upwards into the drift tube of the spectrometer.

We have found that the exact shape of the magnetic fields is not critical for the energy resolution. The field strength at the turn-around point is approximately 0.1 T, the guiding field in the drift tube has a strength of about 0.001 T. The spectrometer is not magnetically shielded. A relatively simple, rectangular arrangement of four large coils used for the compensation of the earth magnetic field serves to adjust the electron beam to the axis of the drift tube.

The energy resolution can be optimized as follows.

(i) The kinetic energy of the anion beam is usually 200–1000 eV, which corresponds to the potential of the entrance tube. The interaction region of the spectrometer must be free of residual electric fields prior to firing the laser and the tube

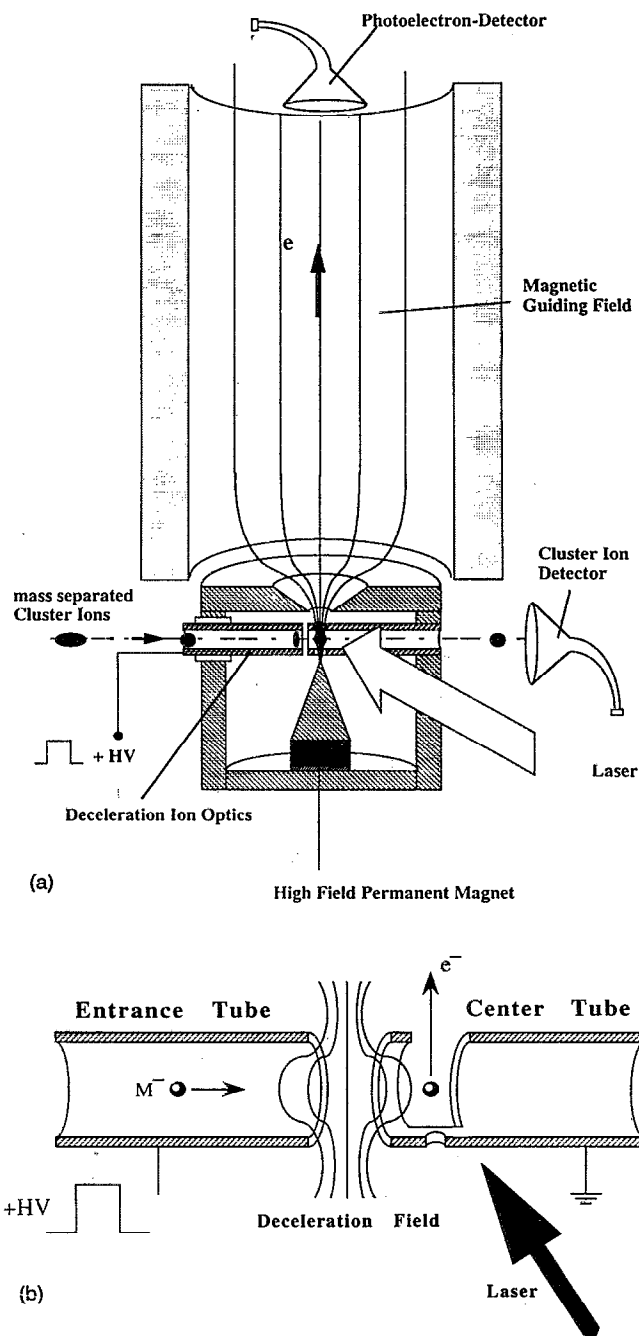


FIG. 1. (a) Schematic view of the source region of the magnetic-bottle TOF electron spectrometer. (b) Enlarged view of the center region of the spectrometer. Also shown is the approximate shape of the deceleration potential (for a detailed discussion see the text).

is switched to ground potential. However, this switching causes high frequency potential oscillations, which lead to corresponding alterations of the kinetic energies of electrons. The oscillations can be minimized by a proper switching technique. It is now performed by a semiconductor switch based on fast field-effect transistors with a low impedance to ground (1Ω). In addition, the connection between the switch (a module outside the vacuum chamber) is as short as possible (0.2 m) and has minimal inductivity and capacity. These improvements result in a significant reduction of the oscillations compared with the earlier design.

(ii) The delay between switching off the deceleration field and the laser pulse is chosen to be as long as possible. The bunch of anions can be decelerated to a minimum of about 10% of the primary beam energy, corresponding to the energy dispersion of the anion beam caused by the acceleration in the Wiley–McLaren TOF mass spectrometer. The faster anions leave the source region if there is a delay until the laser fires, the slower anions remain and the resolution increases with increasing delay. However, the target density decreases at the same time. We achieved a minimum residual energy of less than 2.5% of the primary energy (e.g., at 300 eV less than 8 eV).

(iii) The Doppler broadening depends not only on the residual velocity of the anions, but also on the kinetic energy of the electrons. At low electron kinetic energies the resolution is increased, e.g., if the kinetic energy of the electrons is reduced from 1 to 0.1 eV, the Doppler broadening decreases from 130 to 40 meV. The kinetic energy can be altered by changing the photon energy.

There are other effects that limit the resolution of the TOF instrument.

- (a) The pulse length of the laser (7–25 ns).
- (b) The difference in length of the electron trajectories (0.5%).
- (c) The time resolution of the detector (1 ns).

In all cases the absolute energy resolution increases with decreasing kinetic energy of the electrons, so that we have chosen the photon energy to be about 0.1–0.3 eV above threshold for photoemission of the selected electronic transition. The surfaces within the spectrometer are carefully coated with graphite to minimize surface potentials and, except for the source region, are located at the maximum distance from the electron beam (diameter of the drift tube = 140 mm). With this design we achieved a minimum pass energy of <0.1 eV.

At a relative resolution of 1% this indicates a peak energy resolution of 1 meV, if the Doppler broadening is neglected. However, even with relatively heavy ions, such as Au_2^- , and a minimum primary beam energy (100 eV) residual velocities of less than about 1.5×10^3 m/s are difficult to achieve because of the decreasing anion intensity. For electrons with a kinetic energy of 0.1 eV this corresponds to a Doppler broadening of about 3 meV. Therefore, we estimate the limit of the energy resolution of the spectrometer to be 2–3 meV. The optimum resolution we achieved is 6 meV (see below). A resolution of 10 meV at a relatively high anion and electron intensity (primary beam energy 200 eV, electron kinetic energy 0.3 eV) can be achieved routinely.

The instrument is energy calibrated using known atomic transitions, using two or three transitions at kinetic energies covering the range of the electron spectrum. Nevertheless, the absolute value of the binding energy of a certain feature is uncertain by between ± 20 meV and ± 0.1 eV, depending on the experimental conditions. The uncertainty is mainly caused by changes in the work functions of the surfaces within the spectrometer due to a coverage by the material studied. The uncertainty of the calibration is larger if we study reactive materials (e.g., alkali metals) or insulators (e.g., sulfur).

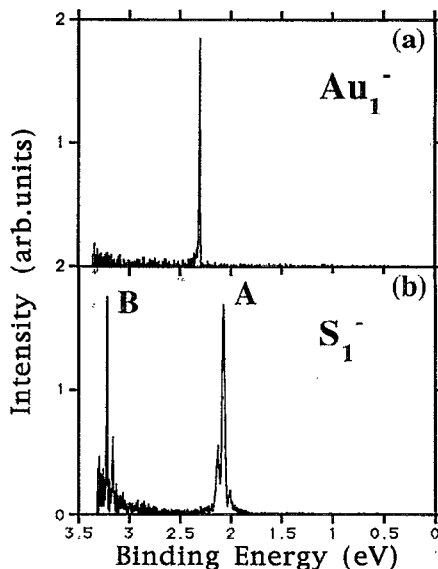


FIG. 2. (a) Photoelectron spectrum of Au_1^- recorded with $h\nu=3.49$ eV photon energy. The FWHM of the single feature is 10 meV. (b) Photoelectron spectrum of S_1^- recorded with $h\nu=3.49$ eV photon energy. The FWHM of feature A is 33 meV, the one of feature B 13 meV.

III. RESULTS

Figure 2(a) displays the photoelectron spectrum of Au_1^- recorded with a photon energy of $h\nu=3.49$ eV (the third harmonic of the Nd-Yag laser). The single observed peak in the spectrum corresponds to the transition from the electronic ground state of the anion 1S_0 into the ground state of the neutral atom $^2S_{1/2}$. The energy of this transition is the electron affinity (2.30 eV)²⁹ corresponding to the binding energy (BE) of the peak. The kinetic energy of the detached electrons is $3.49 - 2.30$ eV = 1.19 eV. The measured full width at half-maximum (FWHM) (10 meV) corresponds to a relative resolution of $\Delta E/E=0.9\%$, which means that the residual velocity of the anions must be smaller than $v_a < 2700$ m/s or a kinetic energy of 7.5 eV. The primary beam energy is 300 eV and the anions are decelerated to less than 2.5% residual kinetic energy.

Figure 2(b) shows a spectrum of S_1^- recorded at the same photon energy as the spectrum of Au_1^- . Because the mass of the sulfur atom is about 1/6th of the mass of the gold atom, the Doppler broadening is about 2.5 times larger at the same residual kinetic energy and it is even more difficult to achieve high resolution for light clusters like C_n^- and Li_n^- . The FWHM of feature A (ground state transition at 2.07 eV BE) is 33 meV and that of feature B (transition into the first excited state of neutral S at 3.22 eV BE) is 13 meV. The observation of the small peaks can be explained by the multiplet structure of both the anion and the neutral sulfur atom.¹⁵ The larger FWHM of the feature corresponding to the electrons with higher kinetic energy (A: 1.42 eV, B: 0.27 eV) demonstrates the linear dependence of the Doppler broadening on $v_{c.m.}$ (see above). The beam energy is 300 eV and the observed Doppler broadening corresponds to a residual kinetic energy of less than 10 eV.

Figures 3 and 4 display examples of vibrationally resolved photoelectron spectra of Au_n^- ($n=2,4,6$) and S_n^- (n

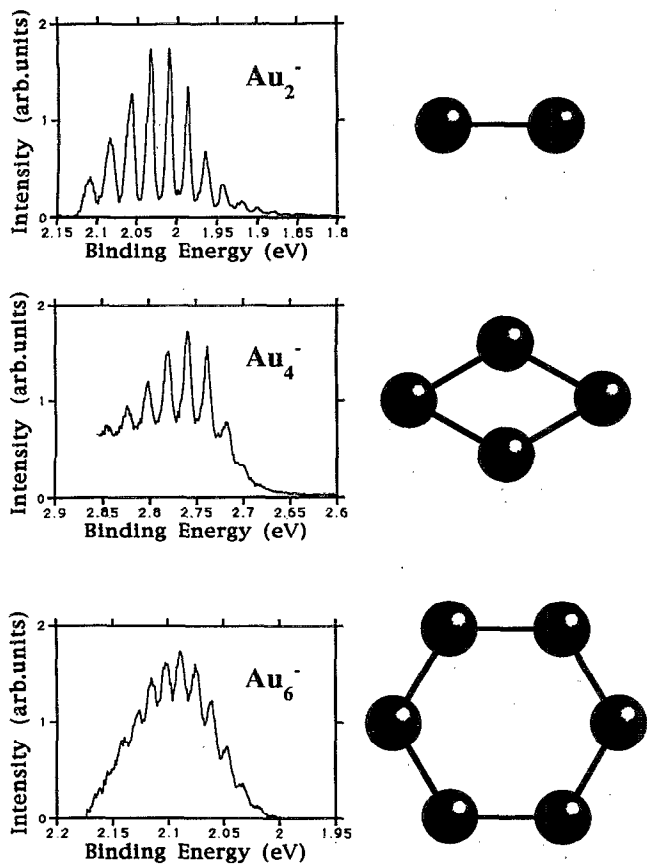


FIG. 3. Expanded view of the photoelectron spectra of Au_n^- clusters with $n=2, 4$, and 6 atoms corresponding to the energy range of the transition from the electronic ground state of the anion into the ground state of the neutral cluster. For each spectrum the photon energy is chosen to obtain a maximum energy resolution (Au_2^- : 2.33 eV; Au_4^- : 2.88 eV; Au_6^- : 2.25 eV). The FWHM of the three largest peaks of the vibrational progression in the spectrum of Au_2^- is 6 meV. For each cluster the geometric structure, which is deduced from a comparison of these experimental findings with corresponding theoretical results, is also shown in the figure (Ref. 30).

$=2,3,4$) clusters. For each cluster an expanded view is plotted corresponding to the BE range of the transitions from the electronic ground state of the anion into the electronic ground (Au_n^- , S_3^-) and low lying excited states (S_2^- , S_4^-) of the neutral. For each cluster we show the geometric structures that are deduced from a comparison of the vibrational fine structure in the spectra with calculated values.^{15,30} An energy resolution of 6 meV (FWHM of the individual vibrational transitions; rotational broadening is neglected) is achieved in the spectrum of Au_2^- , for which a detailed analysis is given in Ref. 4. The gold dimer has a relatively high mass, and the photon energy of 2.33 eV used for the recording of this spectrum corresponds to a low kinetic energy of the detached electrons (about 0.2–0.3 eV). Under these circumstances the resolution is significantly better than for Au_1^- (10 meV resolution at an electron kinetic energy of 1.19 eV).

Apart from the relatively high energy resolution illustrated by the above examples, the spectrometer has several advantages over other experimental techniques.

(a) The high collection efficiency for the photoelectrons

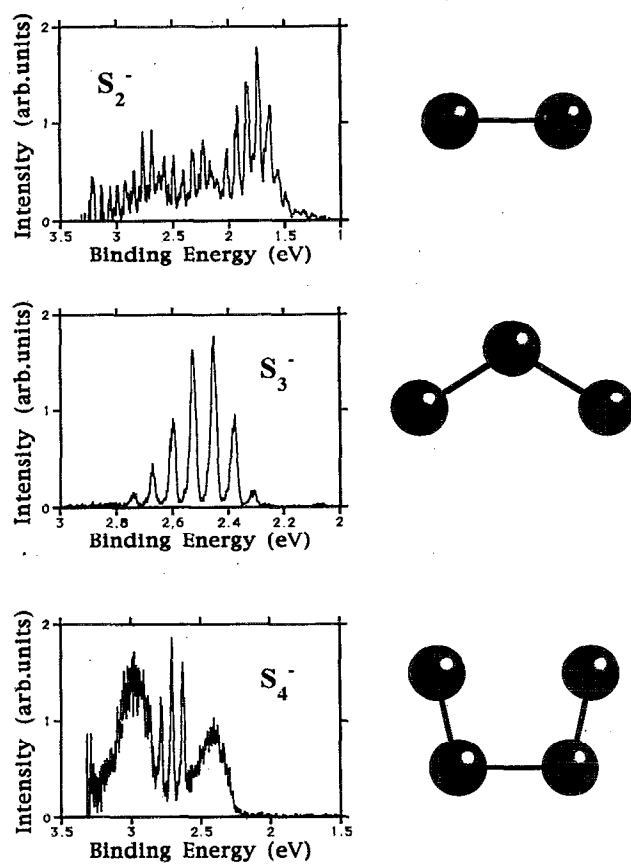


FIG. 4. Expanded view of the photoelectron spectra of S_n^- clusters with $n=2, 3$, and 4 atoms recorded with a photon energy of 2.33 eV. The observed features are assigned to the transitions into the electronic ground and low lying excited states of the neutral clusters. For each cluster the geometric structure, which is deduced from a comparison of these experimental findings with corresponding theoretical results, is also shown in the figure (Ref. 15).

allows the study of clusters and compounds with low relative abundances (at high laser intensity).

(b) Light sources with very high photon energies are available for this type of spectrometer (Excimer laser: 4.0, 5.0, 6.4, 7.9 eV, Nd-Yag laser: 1.17, 2.33, 3.49, 4.66, 5.8 eV, Nd-Yag laser combined with a Raman cell: 6.3, 6.8, 7.3 eV, etc.).

(c) Spectra can be recorded at a very low laser flux (<1 mJ/cm²). This is necessary for the study of larger clusters of, e.g., C and Si to avoid multiphoton processes, which result in a strong background from thermionic emission.

With either a laser vaporization source or a PACIS a spectrum of, e.g., Au_2^- with an energy resolution of 10 meV, can be recorded within 10 min. In our laboratory, the spectrometer has been applied for study of various clusters like Ag_n^- , Au_n^- , C_n^- , Si_n^- , W_n^- , Ni_n^- , Pd_n^- , Pt_n^- , $Ni_nCO_m^-$, $Pd_nCO_m^-$, $Pt_nCO_m^-$, $Ag_nO_m^-$ (laser vaporization source), and Cu_n^- , Na_n^- , K_n^- , Mg_n^- , S_n^- , Al_n^- , Ga_n^- , P_n^- (pulsed arc cluster ion source).

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