

Photoelectron Spectroscopy of Clusters and Adsorbates on Clusters

Chia-Yen Cha, Gerd Ganteför, and Wolfgang Eberhardt

Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-5170 Jülich, Germany

Clusters / Metals / Molecular Structure / Spectroscopy, Photoelectron

The electronic and geometric structure of free metal cluster anions is studied by photodetachment. The cluster anions are produced in a PACIS (Pulsed Arc Cluster Ion Source). From mass separated bunches of anions electrons are detached by a UV-laser pulse. Photoelectron spectra of the detached electrons are measured with a "magnetic bottle" type time of flight spectrometer. First data on Ga_n^- clusters are presented and compared to similar measurements on Al_n^- clusters. At the high resolution (≈ 30 meV) accessible with this experimental set up comparison of the data with calculations delivers new insights into the geometric structure of the particles. A first application of this technique to molecules adsorbed on metal clusters is presented.

I. Introduction

In the last decade the study of the electronic and geometric structure of clusters [1] has become an important area in research. Clusters are new materials and, e. g. in the case of C_{60} , applications seem imminent. Another important commercial application of supported metal clusters is in heterogeneous catalysis. Monodispersed catalysts may be superior to commercial catalysts consisting of particles with a certain size distribution. Results from gas phase chemisorption experiments on clusters [2] show strong variations of reaction rates depending on the exact size of the particles (= number of atoms in a particle). An understanding of the

effects observed in chemical reactivity experiments requires data like the activity, chemisorption energies, the geometry of the particles, adsorption sites and the electronic structure and the type of orbitals relevant for the chemical bond. Due to the problems connected with the preparation and examination of deposited monosized clusters most experiments of this kind so far have been carried out on free clusters.

Photoelectron spectroscopy on anion [3] (photodetachment spectroscopy PDS) is a powerful tool in cluster research. The use of anions solves the common problem of mass selection, which is especially important in the study of

adsorbates. The detachment of the electron is usually much faster than fragmentation processes, thus the electron carries information about the unfragmented anion. Any fragmentation processes induced by the detachment do not influence the data (except via life time effects).

Peaks in the photoelectron spectra correspond to transitions from the ground state of the anion to the electronic states of the neutral particle. Thus, information is gained about the two states involved including the geometry change induced by the detachment. At high resolution [4] vibrational structure in the energy spectrum of the detached electrons may deliver some insight into the geometric structure.

The area of metal and semiconductor cluster research has been strongly dependent on the development of a source for these kind of particles. We present a novel type of a pulsed cluster source which can be used for cluster production of materials in as wide a range as the laser vaporization source [5] (LVS). The PACIS [6] (Pulsed Arc Cluster Ion Source) can produce neutrals as well as negative and positive ions of metal and semiconductor clusters. The vaporization is done using a pulsed electric arc instead of a laser pulse. The advantages of the PACIS compared to the LVS are a higher ion and anion intensity per pulse and low cost. Moreover, we also demonstrate the pulsed vaporization of liquid metals using the PACIS.

The new experimental set up has been used for studies of Ga_n^- and Al_n^- clusters. To our knowledge, this is the first presentation of spectroscopic data on Gallium clusters. Only the dimer [7] has been studied experimentally until now. Very few calculations [7] exist for the small Ga_n clusters. Detailed calculations [8] of the electronic and the geometric structure of neutral Aluminium clusters are available but only scarce data [9] exist allowing for a comparison with theory. In this paper Ga_n^- spectra are compared to the iso-electronic Aluminium clusters. In the spectra of small Al_n^- clusters obtained with a resolution of 30 meV several new electronic states can be distinguished. Finally, first data on molecules adsorbed on metal clusters will be presented.

II. Experimental

The experimental set up is described in detail elsewhere [10]. The apparatus consists of three main components: PACIS, mass spectrometer and electron spectrometer.

1. The PACIS

The Pulsed Arc Cluster Ion Source [6] (PACIS) is comparable to the laser vaporization source [5]. The design of this source is shown schematically in Fig. 1. The difference between the LVS and the PACIS is the method used for vaporization of the target material. For the LVS, a high energy laser pulse vaporizes material from the surface of an rotating rod consisting of the target material. For the PACIS, the laser pulse is replaced by a pulsed high current electric arc eroding the electrodes manufactured of the target material. Both vaporization methods have the advantage to operate in the high pressure environment in the source. The hot metal plasma is produced within the carrier gas (Helium), which causes a fast cooling by heat exchange and energy transfer to the walls of the source body.

There are two different types of source bodies shown in Fig. 1. In the type I (Fig. 1a) source the arc burns within the center of a small ceramic cube. This cube has two channels perpendicularly intersecting each other in the center. The electrodes are inserted from opposite sides into the larger bore. They face each other at the center of the cube leaving a gap of about 1 mm. A carrier gas pulse flows through the second channel and the gap between the electrodes. It leaves the ceramic cube on the opposite side streaming into the extender.

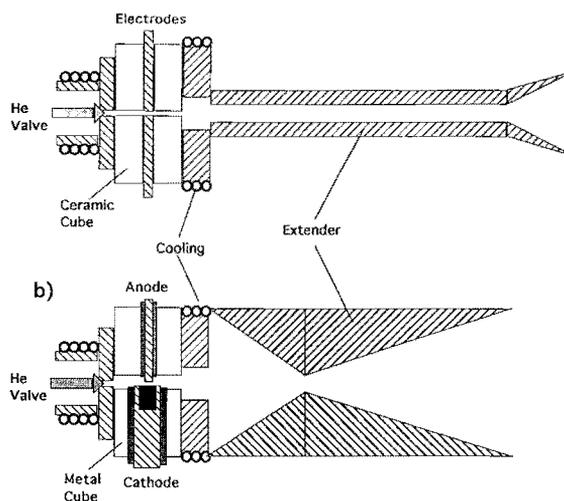


Fig. 1a and b
Schematic view of the two versions of the PACIS used in this experiment: a) type I for conducting solids and b) type II for liquids and alkali metals. The two extenders shown in the figure can be combined with each type. The optimum design of the extenders depends on the material and the charge state of the ions to be produced

Simultaneously with the gas pulse the electric arc is ignited. For about 2–20 μs a current of 5000 A flows between the two electrodes. Only the cathode is eroded. We assume the dominant mechanism for erosion is ion sputtering due to the relative high electric field in the gap (10 kV/cm). The metal vapor and the helium mixes within the discharge and the resulting plasma is flushed into the extender.

In type II of the PACIS (Fig. 1b) the arc burns inside a molybdenum cube by ceramic tubes. The electrodes are insulated against the grounded metal cube by ceramic tubes. The arc burns in a small chamber in the cube. The electrodes are arranged vertically. The upper electrode (anode), which does not erode, is a rod of molybdenum. The lower electrode (cathode) is a rod of molybdenum with a hole at the top. The hole serves as a reservoir for the target material.

One important difference of the PACIS compared to the LVS is the larger amount of energy deposited into the carrier gas. Thus, more effort has to be taken to cool down the mixed helium/metal plasma within the extender. Several different shapes of extenders were compared and depending on the material to be converted into clusters and the charge state desired different designs were found to give the optimum performance. The two examples shown in Fig. 1a and b give reasonable results in most cases.

The high current necessary for the PACIS (~ 5000 A) is delivered by a fast discharge of a capacitor. The capacitor is loaded up to ~ 1000 V between each ignition. A fast semiconductor switch connects the two electrodes to the poles of the capacitor. If the gap is smaller than about 1 mm, the arc ignites. The semiconductor is necessary for correct timing of the discharge. Typical time constants of the discharge are 2–20 μs .

The vacuum system is very similar to a standard setup for a LVS and described in detail elsewhere [10].

2. The Mass Spectrometer

The anions are accelerated by a pulsed electric field within a two stage Wiley McLaren time of flight mass spectrometer [11]. The ions are deflected by 90° by an electrostatic mirror to separate the ion beam and the neutral beam. The anion beam can be alternatively guided directly into the electron spectrometer or can be deviated through a reflectron mass spectrometer. Using the reflectron causes a gain in mass resolution of about a factor of 5 at a simultaneous loss in intensity by about an order of magnitude. The mass resolution of the inline Wiley McLaren time of flight mass spectrometer is about $m/\Delta m = 50$. With the additional use of the reflectron the resolution is enhanced to $m/\Delta m = 250$. The anions pass the electron spectrometer and hit the stop detector.

3. The Electron Spectrometer

The anion bunches of different masses are selected by their time of arrival at the source region of the photoelectron spectrometer. The electrons are detached from a certain cluster anion bunch by an excimer laser pulse. The electron kinetic energy is measured by time of flight. The electrons detached from the clusters are guided by a magnetic field ("magnetic bottle" type electron spectrometer) [12] through the drift region towards the detector. The energy resolution of such a device is usually limited by the Doppler broadening introduced by the velocity of the anions. We have developed a pulsed field technique to stop a selected cluster anion bunch at the interaction region of the electron spectrometer. The energy resolution obtained with this spectrometer is 20 meV at best and 30 meV in the average (for electrons with a kinetic energy lower than 1.5 eV) nearly independent of the cluster mass.

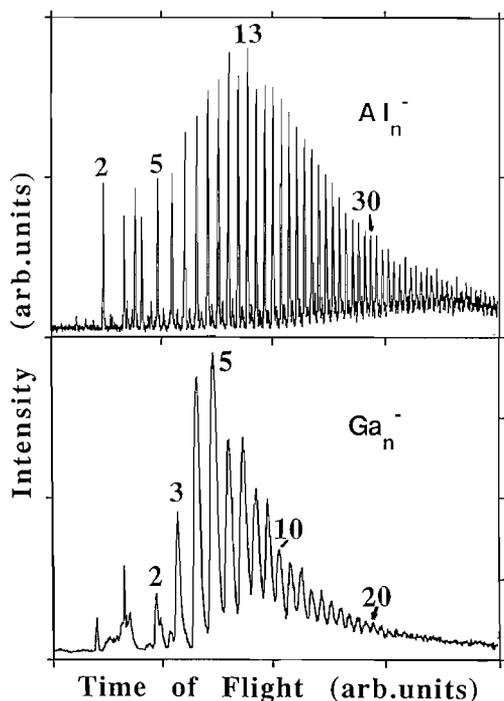


Fig. 2
Typical mass spectra of Al_n^- (type I PACIS) and Ga_n^- (type II PACIS) ions generated by the PACIS. The spectrum of the Al_n^- clusters is recorded using the reflectron spectrometer to increase the mass resolution. The spectrum of Ga_n^- clusters is recorded running the source with very high anion intensity and exhibits strong line broadening due to space charge effects. The two spectra were recorded at different acceleration voltages and are plotted with different zero offset. Both spectra show contamination with oxygen. The mass resolution is limited by space charge effects in the starting area of the time of flight spectrometer

III. Results

Fig. 2a,b display typical mass spectra obtained with type I(a) and type II(b) of the PACIS. The spectrum of Al_n^- clusters is obtained with the reflection spectrometer switched on and demonstrates the gain in mass resolution. The spectrum is similar to Al_n^- mass spectra [9] generated by the laser vaporization source. The lack of intensity modulations due to stability of the anions is a hint for a relatively low internal temperature of the anions (diffusion limited growth). The spectrum of Ga_n^- clusters (Fig. 2b) is measured using the linear time of flight mass spectrometer. The source (PACIS type II) produces a relatively high anion intensity running with Gallium, which yields strong line broadening effects in the mass spectra due to space charge effects. Both spectra exhibit minor contaminations with oxygen.

The total mass integrated current arriving at the stop detector was measured for Cu_n^+ clusters with $n = 1-20$ to be about 0.1 nA at 10 Hz. This corresponds to a total number of 10^6 ions within each bunch of defined mass. The current measured with a Faraday cup shortly behind the skimmer is up to 100 nA at 10 Hz (mass integrated). The large difference is caused by strong losses while passing the beam through the small apertures of the differential pumping stages and the electron spectrometer. The beam is highly divergent due to space charge effects occurring before and during acceleration of the ions. From a careful analysis of the effects we expect to be able to achieve an intensity of >1 nA for a single cluster size at 100 Hz repetition rate and optimized extraction of the ions behind the skimmer.

The photoelectron spectrometer is calibrated using the copper and silver anion with known electron affinities and transitions into known excited states of the neutral atoms. Fig. 3 demonstrates the resolution of the apparatus. Photoelectron spectra of Al_2^- and Al_3^- are presented obtained at a photon energy of 2.33 eV. The binding energy range displayed in the spectrum is limited by the photon energy and the minimum pass energy (~ 20 meV). The electron spectrometer exhibits optimum resolution for electrons with kinetic energies lower than 1.5 eV, thus the photon energy has to

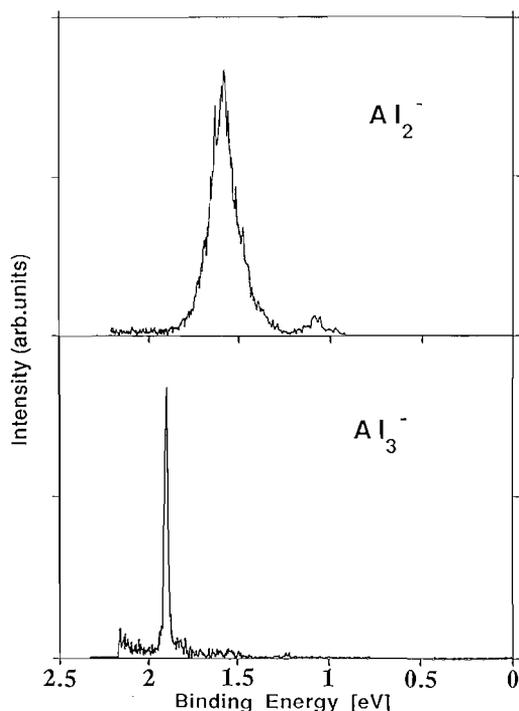


Fig. 3
Photoelectron spectra of Al_2^- and Al_3^- recorded with 2.33 eV photon energy. The experimental resolution is 30 meV. The examined range of the binding energy is 0–2.13 eV. Features with binding energies higher than 2.13 eV cannot be recorded.

be adjusted to the binding energy of the peaks to be studied. The spectrum of Al_2^- exhibits two features: one large peak at 1.6 eV binding energy and a weak feature at 1.1 eV binding energy. The small peak at 1.1 eV is split into two maxima with a distance of 35 ± 5 meV. The spectrum of Al_3^- displays only one narrow line within the examined binding energy range (0–2.15 eV). The measured linewidth corresponds to the experimental resolution of 30 eV.

Fig. 4 displays a comparison of photoelectron spectra of Ga_n^- and Al_n^- with $n = 2-4$. The data are taken at a higher photon energy (3.68 eV). The features displayed in Fig. 3 (Al_2^- and Al_3^-) are reproduced with a lower energy resolution because of the higher kinetic energy of the electrons. Additional lines at higher binding energy are not observed for the two Aluminium clusters, except weak features at 3.2 eV binding energy with intensities comparable to the noise level. The corresponding spectra of the Gallium cluster anions look very similar. The Gallium dimer exhibits peaks nearly at the same positions and the same intensity ratios as the Aluminium dimer. In the case of the Ga_3^- , the intensity ratio of the two features is different from Al_3^- , but the energies are similar. No evidence for states at higher binding energies is found. Both tetramer spectra show one broad feature with nearly no substructure. However, both the energy and shape are quite similar for both clusters.

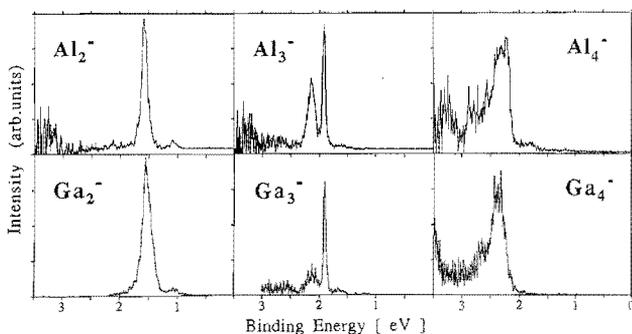


Fig. 4
Comparison of Al_n^- and Ga_n^- photoelectron spectra in the size range $n = 2-4$. The photon energy is 3.68 eV. The examined range of binding energy is 0–3.48 eV and equals the displayed range. The data points of the spectra of Ga_2^- and Ga_3^- are set to zero beyond 2.2 eV and 3.0 eV, respectively, for reason of better visibility. The spectra do not exhibit any significance for features in the spectra at higher binding energy compared to the noise level

Fig. 5 presents the first application of the set up to aggregates consisting of a metal cluster and an adsorbed molecule. A spectrum of Cu_1^- is compared to spectra of $\text{Cu}(\text{OH})_2^-$ and $\text{Cu}(\text{OH})_3^-$. The data of the copper hydroxide anions are taken with the linear time of flight mass spectrometer for intensity reasons. Thus, due to the limited mass resolution, the mass of the particles is known with an uncertainty of about ± 3 amu. Thus, the number of protons in the aggregates is uncertain. The aggregates are produced in the source using Helium with a small amount of water as an impurity. With the adsorption of the molecules the electron affinity increases and also the two d-electron peaks of Cu_1^- at 2.7 eV binding energy shift to higher binding energies. In the case of $\text{Cu}(\text{OH})_3^-$ the main peak at 2 eV binding energy now exhibits a vibrational substructure with a frequency of 500 cm^{-1} .

IV. Discussion

The identification of the features displayed in Figs. 3 and 4 needs elaborate calculations and comparisons and will be published elsewhere [13]. The striking similarity between the two elements is typical for photoelectron spectra of iso-electronic species like Al_n and Ga_n . A similar behaviour is found for Cu_n^- and Ag_n^- clusters [14]. On the other hand,

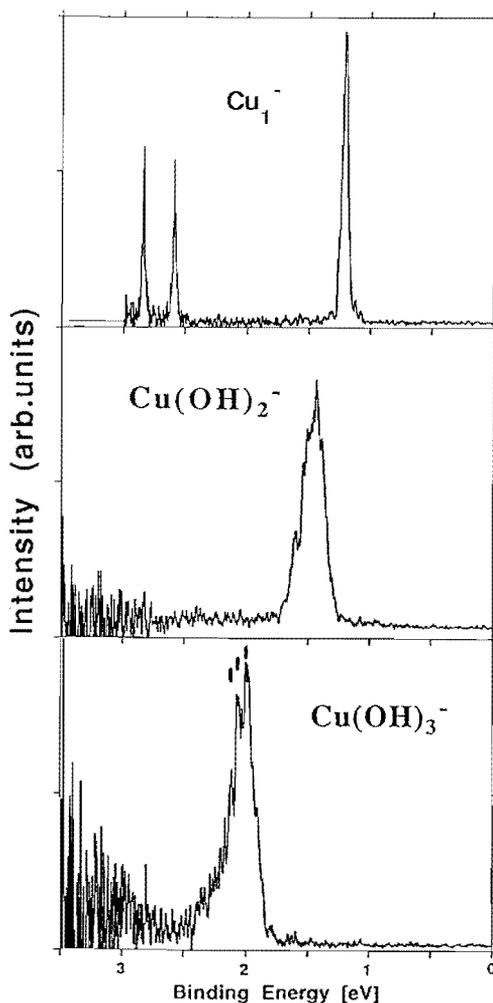


Fig. 5
Comparison of the photoelectron spectrum of Cu_1^- with $\text{Cu}(\text{OH})_2^-$ and $\text{Cu}(\text{OH})_3^-$. The molecules are produced by mixing a small amount of water to the helium carrier gas of the PACIS. For mass separation the linear time of flight spectrometer was used resulting in low mass resolution. The mass of the molecules is uncertain by about ± 3 amu. Thus, the number of hydrogen atoms is uncertain. The photon energy is 3.68 eV similar to the data displayed in Fig. 4. The main feature displayed in the spectrum of $\text{Cu}(\text{OH})_3^-$ exhibits a vibrational substructure (marked with bars) with a frequency of $\sim 500 \text{ cm}^{-1}$

differences in the spectra are expected due to the different sizes of the atoms and the different s-p-hybridization energy.

The splitting of the weak feature in the Al_2^- spectrum at 1.1 eV binding energy (Fig. 3) corresponds very closely to the predicted difference in energy of the two nearly degenerate ground states of the neutral dimer [8]. However, due to the low intensity of this feature, an identification as a transition from the ground state of the anions to the ground state of the neutral seems unlikely. Another possible explanation for the two features is that a small fraction of anions is in a metastable excited state. In that case, the large feature at 1.55 eV binding energy corresponds to the ground state transition. However, we do not observe any change in the intensity ratio of the two features while changing the source parameters. This should alter the population of vibrationally

or electronically excited states. In both cases the final state of the transition corresponding to the feature at 1.1 eV binding energy is the neutral ground state. Thus, independent of the uncertainty of the initial state of the anion, the observed splitting probably mirrors the splitting of the two ground states of the neutral dimer. A comparison with calculated Franck Condon profiles and binding energies will decide between the two possible explanations.

Both trimers (Figs. 3 and 4) exhibit an intense narrow peak at 1.95 eV binding energy. For Al_3^- , a high resolution spectrum [15] using ZEKES yields a line width lower than 15 meV. This narrow line widths indicates a very small geometrical change due to the detachment. The spectra are consistent with the assumption [16] of a regular triangular shape of the neutral and the Al_3^- and the Ga_3^- anions.

An interpretation of the $\text{Cu}(\text{OH})_n^-$ is difficult due to the lack of calculations. The purpose of this first presentation is the demonstration of the power of the method. The two lines in the Cu_3^- spectrum at 2.7 eV binding energy correspond to the detachment of d-electrons, which already poses properties of innershell orbitals. The disappearance of the peaks for the adsorbates must be explained by a shift to higher binding energy, because the d-orbitals of the copper atoms cannot be strongly influenced by the binding except in the form of a chemical shift. The binding energy of the Copper 3d orbitals is shifted to energies higher than the limit of the experiment (3.48 eV). Obviously, this shift can be determined using higher photon energies. These type of experiments will give detailed insight into the formation of the chemisorption bond for molecules on small metal particles which should be of direct relevance to catalysts. The vibrational frequency observed seems to be in rough agreement with Cu–O vibrations found in the oxides [17].

V. Summary

First results of a new experimental set up for photoelectron spectroscopy of metal cluster anions are presented. The suitability of the PACIS used as an pulsed anion source for this type of experiments is shown. The advantages of the PACIS of high ion and anion intensity and low costs are demonstrated. The energy resolution of the "magnetic bottle" type time of flight electron spectrometer has been increased by reducing the Doppler broadening by decelerating the anions before detaching the electrons. This yields moderate energy resolution (30 meV) at high detection efficiencies of the electrons (fast measurements).

For the first time spectra of Gallium clusters have been presented. They exhibit a striking similarity in the size range up to $n = 4$ to Aluminium clusters. The energy splitting of the two nearly degenerate ground states of the Aluminium dimer is directly observed. The trimer data support a model

of a regular triangular shape of the neutral trimer. The geometry change due to detachment of Al_3^- is very small. A first application of the experimental technique to adsorbates yields encouraging data, but further experimental and theoretical work is necessary.

The authors thank Robert Jones for many helpful discussions and the theoretical support of the experiment. We further thank Sybille Krummacher and Paul Bechthold for their experimental support during the built up phase of the experiment. Finally we acknowledge the cooperation with Karl-Heinz Meiwes-Broer and his group.

References

- [1] E. g. Proceedings of the Fifth International Meeting On Small Particles and Inorganic Clusters, *Z. Phys. D* 19+20 (1991).
- [2] E. g. A. Kaldor, D. M. Cox, and M. R. Zakin, in: "Evolution of Size Effects in Chemical Dynamics", Part 2, *Advances in Chemical Physics*, Vol. LXX, eds. I. Prigogine and Stuart A. Rice.
- [3] J. Ho, K. M. Ervin, and W. C. Lineberger, *J. Chem. Phys.* 93, 6987 (1990); O. Cheshnovsky, K. J. Taylor, J. Conceicao, and R. E. Smalley, *Phys. Rev. Lett.* 64, 1785 (1990); G. Ganteför, M. Gausa, K. H. Meiwes-Broer, and H. O. Lutz, *Z. Phys. D* 12, 405 (1989).
- [4] T. N. Kitsopoulos, I. M. Waller, J. G. Loeser, and D. M. Neumark, *Chem. Phys. Lett.* 159, 300 (1989); G. F. Ganteför, D. M. Cox, and A. Kaldor, *J. Chem. Phys.* 93, 8395 (1990).
- [5] V. E. Bondebey and J. H. English, *J. Chem. Phys.* 74, 6978 (1981); T. G. Dietz, M. A. Duncan, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.* 74, 6511 (1981).
- [6] G. Ganteför, H. R. Siekmann, H. O. Lutz, and K. H. Meiwes-Broer, *Chem. Phys. Lett.* 165, 293 (1990); H. R. Siekmann, Ch. Lüder, J. Faehrmann, H. O. Lutz, and K. H. Meiwes-Broer, *Z. Phys. D* 20, 417 (1991).
- [7] U. Meier, S. D. Peyerimhoff, and F. Grein, *Z. Phys. D* 17, 209 (1990), and references therein.
- [8] R. O. Jones, *Phys. Rev. Lett.* 67, 224 (1991), and references therein.
- [9] G. Ganteför, K. H. Meiwes-Broer, and H. O. Lutz, *Phys. Rev. A* 37, 2716 (1988); K. J. Taylor, C. L. Pettiette, M. J. Craycraft, O. Cheshnovsky, and R. E. Smalley, *Chem. Phys. Lett.* 152, 347 (1988).
- [10] C. Y. Cha, G. Ganteför, and W. Eberhardt, submitted to *Rev. Sci. Instrum.* 1992.
- [11] W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.* 26, 1150 (1955).
- [12] P. Kruit and F. H. Read, *J. Phys. E* 16, 313 (1983).
- [13] R. O. Jones, C. Y. Cha, G. Ganteför, and W. Eberhardt, to be published.
- [14] G. Ganteför, Ph./D. thesis, University of Bielefeld, Germany 1989.
- [15] G. Ganteför, D. M. Cox, and A. Kaldor, unpublished results.
- [16] R. O. Jones, private communication.
- [17] D. E. Tevault, R. L. Mowery, R. A. Demarco, and R. R. Smardzewski, *J. Chem. Phys.* 74, 4342 (1981).

Presented at the Discussion Meeting of the Deutsche Bunsen-Gesellschaft für Physikalische Chemie "Reactions in and with Clusters" in Schliersee, Germany, March 29th – April 1st, 1992 E 8026