Photoelectron spectroscopy of Cu$_n^-$ clusters: Comparison with jellium model predictions

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We present a comparison of the electronic level structure of Cu$_n^-$ clusters with the jellium model using photoelectron spectroscopy of metal cluster anions. The spectra are recorded at an energy resolution of 30 meV using photon energies of up to 6.4 eV. We obtain a well resolved picture of the electronic structure of the 4s derived electronic states in the energy region between the localized 3d derived states and the highest occupied molecular orbital. The observed features can be assigned to the 1s, 1p, and 1d shells predicted by the jellium model if ellipsoidal distortions and effects like shake-up processes, multiplet splittings and the s-d hybridization are taken into consideration.

I. INTRODUCTION

The development of the electronic band structure in a small particle with increasing number of atoms is of fundamental interest in cluster research. For the very small aggregates of up to ten atoms spectroscopic data can be compared with the results of quantum chemical calculations[1] treating each cluster as an individual molecule. However, this approach is not appropriate to describe the variation of the structure of these particles on a larger size scale. To compare general trends and basic symmetries for different systems the use of a simple model is in many cases more helpful to achieve a qualitative understanding of the fundamental forces and symmetries.

A successful model for the description of the properties of metal clusters with delocalized valence electrons is the jellium model[2–6] (JM). Various experimental observations[5] like the magic numbers observed in mass spectra of alkali clusters can be explained using this model. However, recent high quality spectroscopic data[7] reveal details of the electronic and geometric structure of these particles which in many cases cannot be described by the JM. Therefore, the validity of the jellium model (electronic shell model) is a matter of considerable discussion in literature.

Here we try to address this issue by presenting photoemission data from mass selected Cu clusters containing a well defined number of atoms. Within the framework of the JM the Cu 4s electrons are delocalized in the geometric boundaries of the cluster. Therefore, in the range of binding energies where the density of states in the Cu clusters is dominated by 4s derived states,[8] the electronic structure should exhibit a certain similarity to the one of alkali metal clusters. If the cluster is spherical,[2–5] the eigenstates of the potential are degenerate electronic shells with a defined angular momentum resulting in a shell structure with shell closings at $n = 2,8,18,20,...$. However, the pronounced even–odd alternation[2] of the ionization potentials (IP's) can only be understood if the highest occupied molecular orbital (HOMO) is nondegenerate. The JM can explain the even–odd alternation, if a reduction of the degeneracy of the shells is introduced by lowering the symmetry of the cluster.[4,6]

We obtain a picture of the development of the electronic states of the Cu$_n^-$ clusters as the cluster size increases atom by atom from 1 to 18 atoms. We note that the direct comparison with photoemission data allow for a much more stringent test of a model than the verification of experimental data of ionization potentials, electron affinities, and the overall stability of the clusters.

Clusters of the alkali and the coinage metals have been studied previously by photoemission.[8–11] Hoe et al.[9] presented photoelectron spectra of Cu$_n^-$ clusters with $n = 1$–10 and for binding energies up to 3.35 eV at an instrumental resolution of 6–9 meV. However, due to the relatively low photon energy only a part of the relevant s-derived states of the Cu$_n^-$ clusters was revealed. Taylor et al.[10] used excimer laser radiation with $h\nu = 7.9$ eV for their experiment and were able to record even the 3d-derived states beyond 4 eV binding energy. However, due to their limited energy resolution they were not able to resolve the fine structures of the 4s-derived orbitals. McHugh et al.[11] studied alkali clusters using photoemission. In their experiment the photon energy and the experimental energy resolution are sufficient to resolve the fine structures predicted by the jellium model. However, the presented alkali cluster spectra with $n > 4$ display only features much broader than their experimental resolution and no fine structure is resolved for the larger clusters (e.g., K$_n^-$ with $n = 13$–19).

With our new experimental setup,[12] we can obtain photoelectron spectra of mass-selected metal cluster anions at sufficient energy resolution and high photon energy to uncover the electronic fine structure of each cluster. Therefore, we consider our present contribution as a further step in the understanding of the electronic structure of metal clusters. As will be shown below, we were able to resolve the splitting of features assigned to the 1p and 1d electronic shell into subshells. The splitting can be related to the symmetry of the cluster. We observe additional peaks in the spectra of the Cu$_n^-$ clusters with an odd number of electrons. These features can be assigned to multiplet splitting caused by the two unpaired electrons occupying different orbitals in the neutral cluster.
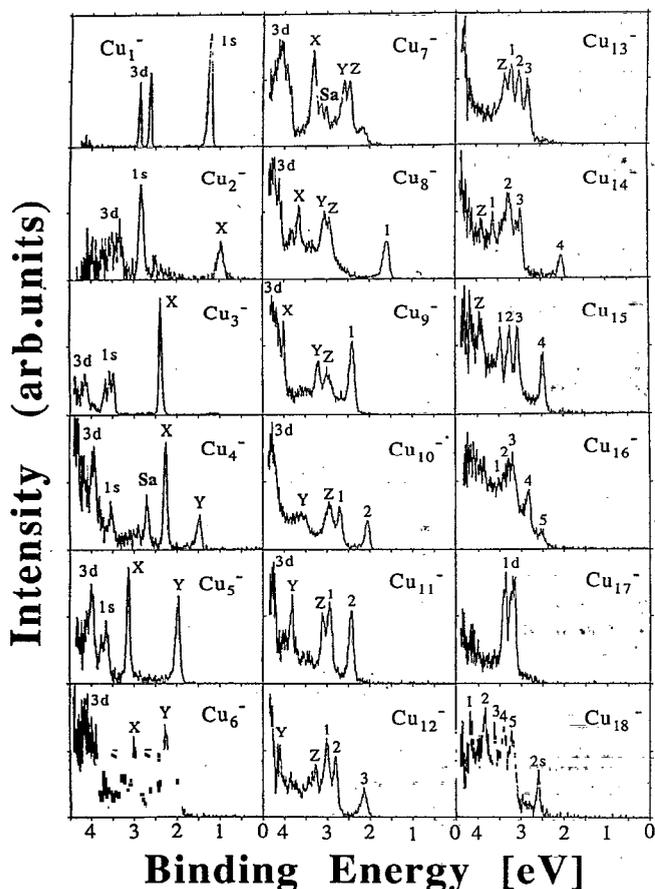
FIG. 1. Photoelectron spectra of Cu_n^- cluster anions. The photon energy is 5.0 eV (KrF). The features corresponding to the localized atomic $3d$ electrons are marked $3d$. Satellites assigned to shake-up processes or multiplet splitting are marked Sa. The features corresponding to the jellium sublevels of the $1s$, $1p_{x,y,z}$, $1d_{1,2,3,4,5}$, and $2s$ shell are marked $1s$, x, y, z, 1, 2, 3, 4, 5, and $2s$, respectively. For Cu_{17}^- the five $1d$ sublevels are degenerate to a double peak marked $1d$.

In the following our experimental results on Cu clusters will be presented and qualitatively compared with JM predictions.

II. EXPERIMENTAL SETUP

The experimental setup is described in detail elsewhere.[12] The cluster anions are generated by a pulsed arc cluster ion source (PACIS) (Ref. 13) and mass-separated using a time-of-flight mass spectrometer. Within the electron spectrometer a selected bunch of anions of defined mass is nearly stopped by a pulsed electric field and then irradiated by an ultraviolet (UV) laser pulse. The photon energy is either 5.0 eV (KrF excimer laser) or 6.424 eV (ArF excimer laser). The kinetic energy of the detached electrons is measured by the time-of-flight method using a "magnetic bottle"-type spectrometer. A maximum energy resolution of 20–30 meV is achieved.

III. RESULTS AND DISCUSSION

Figure 1 displays photoelectron spectra of Cu_n^--clusters with $n = 1$–18. The photon energy is 5.0 eV

(KrF laser). The data are in agreement with previous measurements,[8–10] if the differences in energy resolution and photon energy are taken into consideration.

The spectra displayed in Fig. 1 contain the desired information about the electronic structure of the clusters. According to the quantum mechanical accurate picture the features in the spectra correspond to transitions from the electronic ground state of the anion into electronic states of the neutral cluster. The peak located at the lowest binding energy corresponds to the transition into the neutral electronic ground state. For a detailed analysis of the spectra geometry effects (Franck–Condon principle) and the selection rules have to be taken into consideration. Based on quantum chemical calculations features observed in the spectra of the very small clusters ($n < 5$) can be assigned to certain electronic states of the neutral clusters.[1,14] However, a discussion of the experimental results using this exact interpretation and a comparison with the results of quantum chemical calculations is not the issue of this paper and will be presented elsewhere.

In the present contribution we will discuss the spectra qualitatively using the single particle picture as the first approximation. According to this model each feature in a photoelectron spectrum corresponds to photoemission from an occupied single particle orbital in the cluster. This model reflects basically the selection rules governing photoemission processes, but neglects final state interactions. Therefore, the experimental spectra usually exhibit additional peaks compared with the predictions of the single particle picture. These additional features and the apparent splittings of the photoemission features can be explained by *shake up* processes, *multiplet splittings*, and the $4s/3d$ *hybridization* (for Cu), which are first order corrections of this model.

Shake up processes correspond to the simultaneous excitation of bound electrons accompanying the photoemission process. The final state of the neutral cluster exhibits a single hole due to the detached electron and one or several electron–hole pairs corresponding to electrons excited into higher unoccupied orbitals. The energy necessary for the excitation is taken from the kinetic energy of the outgoing electron. Therefore, shake up processes cause the appearance of additional features located at higher binding energy compared to the direct emission line. The intensity of the shake up features with respect to the direct emission line depends on the overlap between the wave functions of the negative ion and the neutral system. For atoms, shake up features with relative intensities of more than 50% of the direct emission line are found.[15]

Multiplet splitting is caused by the spin–spin interaction of the electrons in the cluster. If two electrons occupy two different single particle orbitals within the particle, these two unpaired electrons can combine to a singlet or a triplet state. For example, if the cluster anion has an unpaired electron occupying the outermost orbital, detachment of an electron from one of the deeper single particle orbitals creates a neutral cluster with such two unpaired electrons. In this case photoemission from any orbital occupied by two electrons yields a singlet and a triplet peak

in the photoelectron spectrum. The splitting between the two peaks corresponds to the spin–spin interaction energy. For metal clusters this energy is expected to decrease, because the average geometric distance between any two electrons in delocalized orbitals increases with increasing cluster diameter.

Hybridization is the mixing of different symmetries in certain orbitals. For Cu, the density of states in the valence band corresponds mostly to $3d$, $4s$, and $4p$ derived single particle orbitals. $3d$ derived orbitals are localized and therefore the JM is most likely not valid for such states. From recent experiments the energetic range of the $3d$ band in small Cu clusters is known.[8] The $3d$ derived density of states corresponds to a relatively high photoemission signal covering the range between 2–5 eV below the binding energy (BE) of the HOMO. The orbitals between the HOMO and the upper edge of the $3d$ band (at about 4 eV BE, Fig. 1) are most likely $4s$ derived states. However, a single particle orbital can exhibit a mixed $3d$ and $4s$ symmetry. Orbitals located close to the $3d$ band might lose their dominant $4s$ character. This $3d/4s$ hybridization might cause a splitting of a $4s$ single particle orbital.

We restrict our discussion to features with binding energies above the $3d$ band in the clusters. In the following we will try to gain a qualitative interpretation of the spectrum of each one of the Cu_n^- clusters using the JM and taking the secondary effects mentioned above into account where appropriate.

The spectrum of Cu_1^- exhibits two features (marked $3d$, $1s$). The peak at 1.24 eV BE ($1s$) corresponds to photoemission from the $4s$ orbital of the anion occupied by two electrons. The feature is 2.7 eV BE ($3d$) is assigned to photoemission from the $3d$ orbital occupied by ten electrons. The splitting is caused by the spin–orbit interaction of the $3d$ electrons. Feature $1s$ is assigned to the $1s$ shell of the JM filled with two electrons, while feature $3d$ cannot be assigned using the JM only.

For three electrons (Cu_2^-), the JM predicts two features, the filled $1s$ level and the $1p$ level occupied by one electron. Also, the BE of the $1s$ level should be increased compared to the two electron system. Indeed, the spectrum of Cu_2^- exhibits two main features (marked $1s$, x) with the $1s$ peak shifted by 1.5 eV compared to Cu_1^-. An additional broad feature beyond 3.3 eV BE is assigned to the $3d$ states of the atom developing into the $3d$ band of the bulk. We note, that feature $1s$ and x correspond to the bonding σ and antibonding σ^* molecular orbital of the dimer. The symmetries of the molecular orbitals exhibit a certain similarity to the jellium orbitals ($\sigma \leftrightarrow s$; $\sigma^* \leftrightarrow p$).

The four electron system (Cu_3^-) should exhibit again two features only. One more electron is filled into the $1p_x$ orbital. Indeed, the spectrum of Cu_3^- displays two features with about an intensity ratio of 1:1 (marked $1s$, x). The broad peak beyond 4 eV BE is assigned to the $3d$ band. The states corresponding to the atomic $3d$ orbitals dominate the cluster spectra beyond 4 eV BE in the regime of $n = 3$–10. The $3d$ band shifts with increasing cluster size towards higher binding energy and vanishing at about $n = 14$ be-
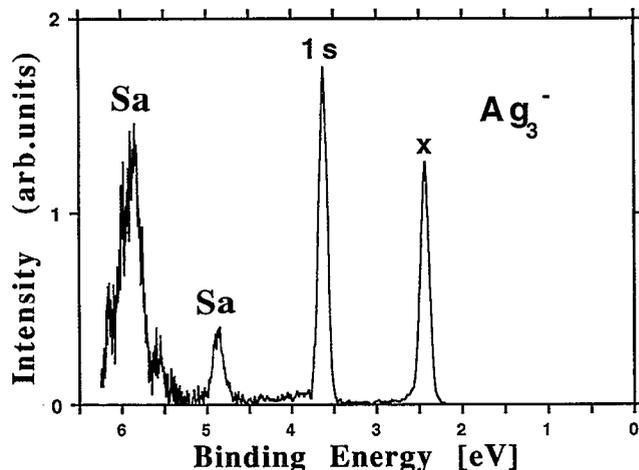

FIG. 2. Photoelectron spectrum of Ag_3^-. The photon energy is 6.42 eV (ArF). The two features at high binding energy (marked Sa) are assigned to excited states of the neutral trimer corresponding to the $4s \rightarrow 4p$ excitation in the atom. The features assigned to the jellium orbital $1s$, $1p_x$ are marked $1s$, x, respectively.

yond the energy range accessible with 5 eV excitation energy (KrF).

The feature marked $1s$ in the spectrum of Cu_3^- splits into three sublevels in disagreement with the JM. A possible explanation is a mixing (hybridization) with the $3d$ states located at 0.5 eV higher BE. For silver, the corresponding $4d$ states are located at ~ 2 eV higher BE. Thus, the $1s$ state should exhibit less perturbation by s–d-hybridization. Indeed, the photoelectron spectrum of Ag_3^- exhibits only a single $1s$ level in agreement with the JM (Fig. 2). For the larger clusters, a clear separation of the $1s$ orbital and the $3d$ levels is difficult but tentatively assigned in Fig. 1. We note, that according to quantum chemical calculations[16] Ag_3^- is a linear molecule and the two features ($1s$, x) observed in the photoelectron spectrum correspond to electronic states of the same symmetry as in the case of the dimers (Cu_2^-, Ag_2^-).

From Cu_3^- to Cu_7^- the $1p_y$ and $1p_z$ sublevels (indicated in Fig. 1 as y,z) are filled with up to 4 additional electrons. Half-filled sublevels appear with reduced relative intensity (e.g., feature y in the spectrum of Cu_4^-). The $1p$ shell is split into sublevels indicating the deviation of the small cluster from a spherical symmetry. Even for Cu_7^-, which corresponds to an electronically closed shell, the $1p$ orbitals are nondegenerate. There is a splitting of about 1 eV between the $1p_x$ and the nearly degenerate $1p_y$ and $1p_z$ sublevel. This is in disagreement with most of the JM calculations which predict a triply degenerate $1p$ level for an 8 electro cluster.[2–6]

The spectra of Cu_4^-, Cu_6^-, and Cu_7^- exhibit additional features (marked Sa) which cannot be explained within the JM. For these clusters the number of observed peaks is too large compared with the number of available electrons and the maximum possible number of occupied orbitals. For cluster anions with an odd number of electrons (i.e., Cu_4^- and Cu_6^-) the most straightforward explanation is

multiplet splitting. These clusters have an unpaired electron in the outermost orbital. After ejection of one electron from a filled orbital the cluster has two unpaired electrons, which may arrange to a singlet or a triplet state. The intensity ratio of the different multiplet components (1:3) as well as the relative energy splitting and the decrease of this splitting with increasing cluster size all are in support of this interpretation.

In order to explain the Cu_7^- spectrum we have to invoke shake up processes as they are also observed for the Cu_1^- and Ag_3^- and other species. Shake-up features appear to first order at a certain energy loss relative to the main line and the features marked Sa exhibit this behavior.

Within the JM the $1p$ shell is completely filled starting with Cu_7^-. The ninth electron of Cu_8^- has to be filled into the next shell ($1d$). According to the JM, the spectrum of Cu_8^- should exhibit about the same features as the spectrum of Cu_7^- (shifted slightly towards higher BE) plus one additional peak at low BE. This is in good agreement with the experiment (Fig. 1, features X, Y, Z, 1). In Fig. 1 the sublevels of the $1d$ shell are marked 1, 2, 3, 4, 5.

From Cu_8^- to Cu_{17}^- the jellium $1d$ orbital is filled with up to ten electrons, whereas the $1p$ sublevel merge successively into the $3d$ band. In most spectra (e.g., Cu_{13}^- and Cu_{15}^-) the individual $1d$ sublevels are quite well resolved. For Cu_{14}^- and Cu_{16}^- the relative distance between the levels is too small to be separated into individual features. For Cu_{17}^- a narrow double peak is observed and assigned to the shell closing of the $1d$ jellium shell. The relatively high degree of degeneracy of the electronic states points to a high degree of symmetry of the atomic coordinates. Possibly Cu_{17}^- is the smallest cluster with a symmetry close to a sphere. For Cu_{18}^- the $1d$ band splits again into sublevels and an additional feature at low BE is assigned to the single electron in the $2s$ orbital.

Figure 3(a) displays the measured BEs of the features assigned to electronic shells according to the JM. We remind, that these BEs are extracted from photoelectron spectra of negative ions and therefore correspond to excited states of the neutral cluster in the geometry of the anions.

We compare the data displayed in Fig. 3(a) with the calculated level structure of neutral Na_n clusters[17] [Fig. 3(b)]. The energy gaps between electronic states are larger by a factor of 2 for the Cu_n^- clusters compared to the Na_n clusters. Apart from this general scaling behavior a certain similarity can be found between these calculations and our measured peak energies. For the $1p$ shell closing (Na_8, Cu_7^-) the calculations predict a splitting into two orbitals by ~0.5 eV. The orbital at lower BE is doubly degenerate. For Cu_7^- our spectrum exhibits three features assigned to the $1p$ shell. The $1p_x$ level is separated from the $1p_y$ and $1p_z$ orbital by ~1 eV, while $1p_y$ and $1p_z$ are nearly degenerate very similar to the calculations for Na_8. For $n=13$ the calculations predict a shift of one of the $1p$ sublevels to lower BE very close to the $1d$ shell. We also observe this behavior, e.g., for Cu_{13}^-, where a band of 4 peaks is formed from one $1p$ sublevel and three $1d$ orbitals. However, before we carry this comparison too far we have to note that
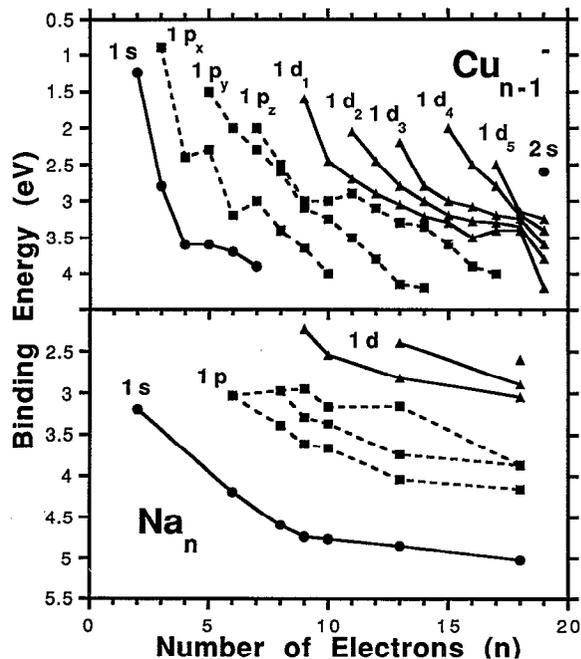

FIG. 3. (a) Binding energies of the features of the spectra shown in Fig. 1 assigned to electronic shells according to the jellium model. Levels of similar symmetry predicted by the model are connected. (b) Kohn–Sham one-electron eigenvalues as a function of the number of atoms in Na_n clusters. The assignment to jellium sublevels corresponds to the dominant component of the eigenstate (taken from Ref. 17).

the two systems are quite different because of the additional interaction with the $3d$ electrons in Cu. Therefore, detailed high quality calculations on Cu_n^- are needed.

IV. SUMMARY

We presented photoelectron spectra of Cu_n^- clusters with $n=1–18$. The features in the part of the spectra, which are predominantly of s-like character ($4s$ derived orbitals) are qualitatively assigned to JM electronic shells. Nearly all observed peaks can be assigned if additional effects such as s–d hybridization, multiplet splittings, and shake up processes are taken into account. This is totally different from the case of small Al_n^- clusters,[18] where no similarity with JM structures can be found.

The qualitative agreement of the spectra with JM predictions supports the picture that the valence electrons in the outermost orbitals corresponding to the $4s$ atomic orbitals are totally delocalized. This is one condition necessary for the development of metallic properties. However, as displayed in Fig. 1, the clusters with up to 18 atoms exhibit gaps of 0.2–1.5 eV between the individual electronic shells and therefore should behave like semiconductors. With further increasing cluster size the density of states increases while the distance between electronic levels decreases. The gap will vanish and a transition into metallic behavior is expected. Thus, our experiment has to be extended to larger clusters to study this transition.

ACKNOWLEDGMENTS

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