

INDIAN INSTITUTE OF TECHNOLOGY MADRAS



SEMINAR PRESENTED FOR CY 653 ON
PHOTOELECTRON SPECTROSCOPY OF
COPPER CLUSTERS. DATE: 24/02/2006

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1) INTRODUCTION:

From a long time people have shown their interest in the spectroscopic, structural and chemical properties of small metal particles. A major goal of this work has been to characterize the evolution from the molecular to the bulk metallic state, and ultimately to forge a link between the molecular quantum chemistry and surface science. Thus much effort has been directed toward examining the dependence of well-defined electronic structure properties on the number of atoms comprising the cluster. Till mid eighties people had been working on the theoretical aspects of calculating the metal cluster electron affinities and ionization potentials and their approach toward the bulk work function with increasing cluster size. In addition numerous calculation has been investigated the energy gap between the HOMO and LUMO as a function of the cluster size and development of the bulk electronic band structure defining features of the metallic state.

In contrast relatively few experimental data are available to test these methods. The scarcity in large part has been due to the difficulty in extracting information concerning particles of definite size from the samples having cluster distributions.

Smalley and co-workers in the mid-eighties have investigated the laser - fluence dependences of relative cross sections for the photo detachment from the Cu_n^- ($7 \leq n \leq 30$) anions to obtain estimates of electron affinities.

The work of Brechignac *et al* on the auto ionization of mercury clusters provides the direct experimental measurements of the development of the electronic band structure in the metal clusters of definite size.

Laser photo electron spectroscopy of negative ions potentially provides a very powerful technique for investigating the electronic structures of size dependence on the metal clusters. The measurement photo electron kinetic energies yield information regarding the Franck Condon factors for electron attachment, leading to precise determination of adiabatic electron affinities. In addition, the experiment provides a direct probe of the low lying excited electronic states of the neutral cluster.

Here we describe a simple method of producing continuous beams of the transition metal cluster anions at the low temperature using a cold cathode dc discharge in a flowing after-glow ion source, which produces metal ion beams at intensities ($10^{-13} - 10^{-13}$ A) which is adequate for spectroscopic analysis.

This source has been used to measure the negative ion photo electron spectra of Cu_n^- , $n=1-10$.

2) EXPERIMENTAL ASPECTS:

Copper clusters are prepared from a flowing after glow ion source with a cold cathode dc discharge. In the discharge source, metal atoms and ions are sputtered from the cathode by bombardment with Ar^+ . Further interactions with the dense plasma yield metal anions which can form large clusters by ion molecule reactions during 10^{-2} s residence time in the in the flow tube. The anions are then extracted to a low pressure region and are mass selected using a Wien filter. The beam of selected anions are then decelerated and crossed by the intra-cavity beam of a cw argon ion laser tipped at the magic angle yielding the photo detachment signal which is proportional to the photo detachment cross section. A small fraction of the photo detached electrons are energy analyzed at a resolution of $\sim 10\text{meV}$ (80 cm^{-1}) by a hemispherical electrostatic monochromator and detected by a 2D position sensitive detector. The simple design presented in the FIG.(1):

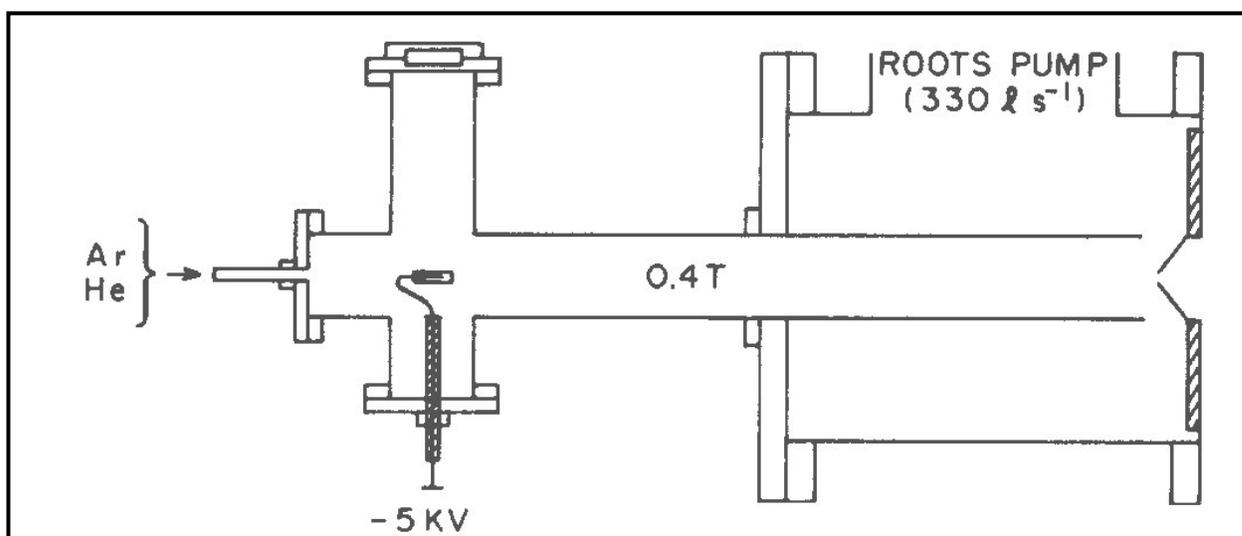


FIG.1. *Cross-sectional scale drawing of the flowing after-glow ion source equipped with a cold cathode dc discharge for the production of the metal clusters.*

The cathode consists of a 1 in. long tube of $\frac{1}{4}$ in. o.d. OFHC copper positioned on the axis of the 1.8 in. i.d. flow tube. Mechanical support and electrical contact are provided by a $\frac{1}{8}$ in. diameter OFHC copper wire passing through the cathode. The wire is insulated by alumina tubing secured to vacuum seal. The stain less steel flow tube serves as the anode, and the

(~ 60 STP cc s^{-1}) gas flow provides the directionality. To minimize heating, the external portions of the 30-50 cm long flow tube and cathode assembly are wrapped with water-cooling coils. The cathode is negative biased at 5KV with respect to the grounded flow tube, producing a discharge current of 30mA in the mixture of 10%- 20% Ar in He at a gas pressure of 0.4 torr. In order to take care of the impurities, mainly the metal oxides, the helium gas was passed through the liq. N_2 cooled molecular sieves and UHP Ar was used.

3) RESULTS:

A) Metal cluster anion production

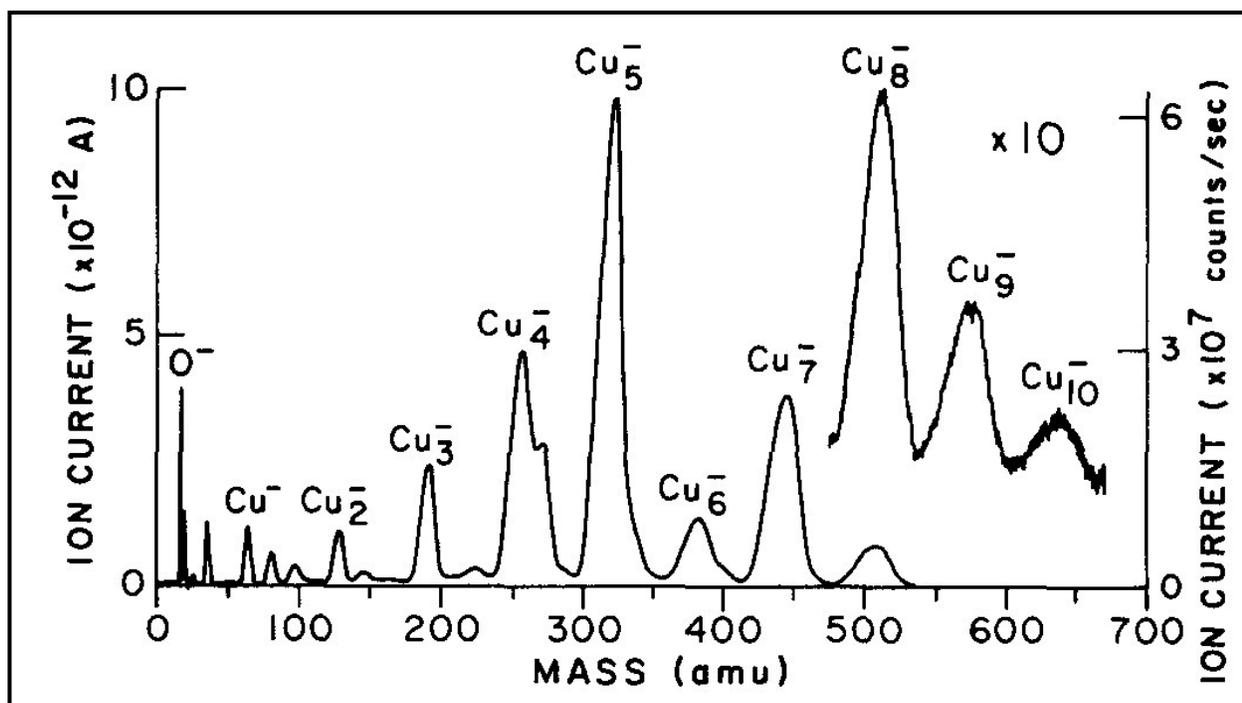


FIG.2. Mass spectrum of Cu_n^- anions prepared in the cold cathode dc discharge source.

Fig. 2 displays a typical mass spectrum of the copper clusters prepared in the above method. Anion abundances increase with cluster size, from 1 Pa for Cu^- to 10 Pa (6×10^7 ions/sec) for Cu_5^- . Intensities of higher clusters display a reproducible maximum at Cu_7^- . Anions of more than ten atoms are definitely produced but they are difficult to detect due to the reduced

resolution of the filter at higher masses. Between Cu_4^- and Cu_8^- , the mass spectrum displays the odd>even intensity alternations.

B) Photoelectron spectra of copper cluster anions:
General observations

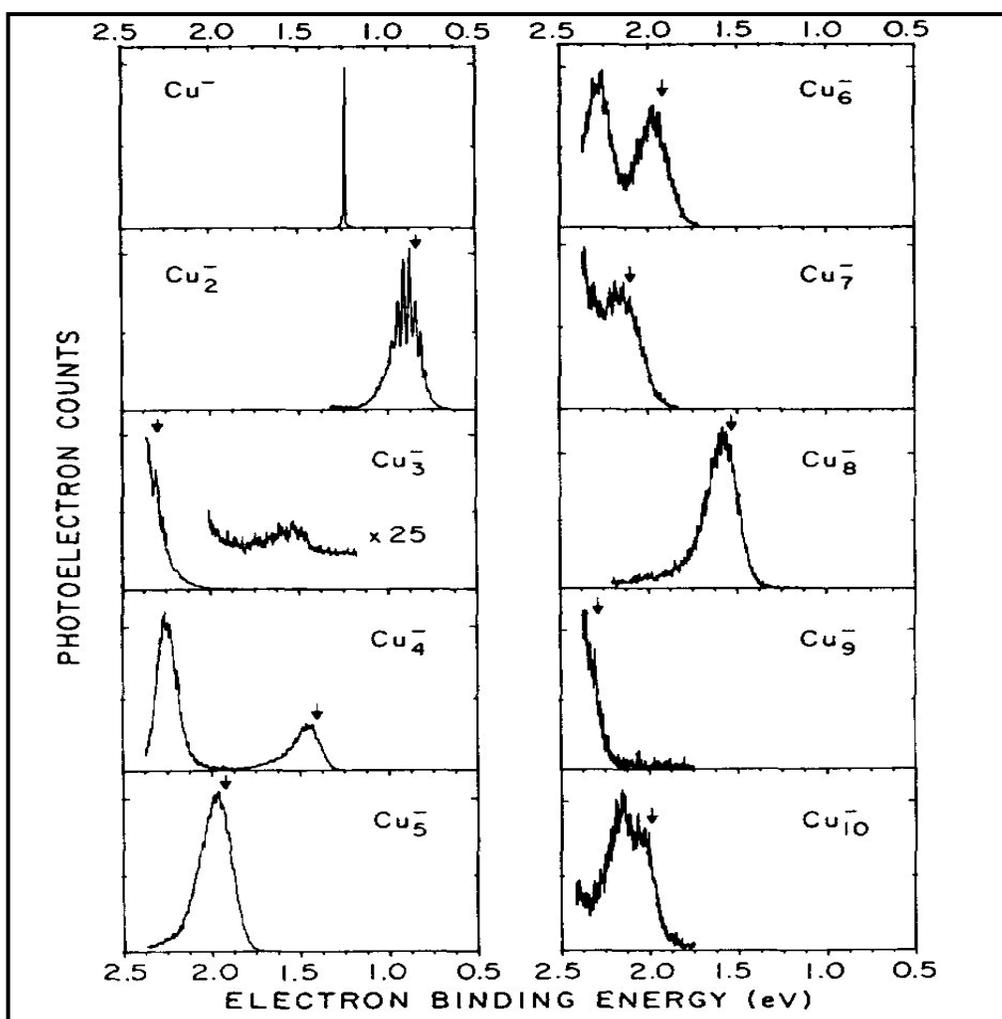


FIG.3. Photoelectron spectra of Cu_n^- obtained at 488 nm at an instrumental resolution of $\sim 10\text{meV}$.

Fig. 3 shows the negative ion photoelectron spectra of Cu_n^- , $n=1-10$. The data were obtained at excitation energies of 2.540eV (488nm); the five times more intense 488 nm Ar^+ laser line was used to collect all the data in the $0-2.2\text{eV}$ region. Of the two photo detachment transitions from a given anion level, the one terminating at a lower energy state of the neutral molecule appears to the right. The photoelectron counts vary for different spectra and range from

3000 for Cu_5^- to 20 for Cu_9^- . These differences are due to the factors such as anion abundances and laser intensity.

It is apparent from the figure that the ten systems studied here all photo detach in the 0-2.4eV region accessible for this region. The positions of the intensity maxima of the lowest energy bands determine the vertical electron binding energies of the anions, except for the case of Cu_3^- , whose weak peak is definitely an electronic hot band. The vertical binding energies correspond to the transitions from the ground electronic state of the anion to the ground electronic state of the neutral molecule in the un-relaxed geometry, and are listed in Table 1. The arrows indicate the adiabatic electron affinities, which correspond to the transitions from the ground electronic state of the anion to the ground electronic state of the neutral molecule in the equilibrium geometry. The results are listed below.

	Vertical detachment energy (eV)	Adiabatic electron affinity (eV)	Bandwidth (meV)	Cun excited state
Cu	1.235±0.005	4	1.389, 3.786
Cu2	0.89±0.001	0.842±0.010	80	2.534
Cu3	2.35–2.55	2.30–2.50
Cu4	1.45±0.02	1.40±0.05	80	0.80±0.02
Cu5	1.97±0.02	1.92±0.05	90	>0.60
Cu6	1.97±0.02	1.92±0.05	90	0.31±0.02
Cu7	2.15±0.02	2.10±0.05	100	≥0.20
Cu8	1.58±0.02	1.53±0.05	90	>1.00
Cu9	2.35–2.65	2.30–2.60
Cu10	2.04±0.02	1.99±0.05	80	0.14±0.03

TABLE I. Cu_n^- photoelectron results.

The results display two important trends. First there is an increase in in electron binding energies with cluster size from 0.9eV for Cu_2^- to 2.0 eV for Cu_{10}^- . In addition there is an alternation between the electron binding energies of consecutive odd and even clusters, with those containing odd and even

clusters, with those containing odd numbers of atoms having higher energies. The equal electron binding energies for Cu_5^- and Cu_6^- provide the sole exception to this pattern.

Additional features are shown in some of these spectra. Electronic structure is cleanly resolved in the case of Cu_4^- and Cu_6^- , and at least partially in the Cu_7^- and Cu_{10}^- spectra, yielding excited electronic states for the neutral clusters. A comparison among the band intervals in these four spectra indicates that the energy of the lowest observed excited state of the neutral molecule decreases with respect to the ground state as the cluster grows.

Bandwidths in the photoelectron spectra of the molecular anions, listed in the table are almost constant. Since the ground electronic states of the neutral molecule are expected to be bound with respect to dissociation, by $\sim 1\text{eV}$, or more, excitation at 488nm cannot, in general, access the dissociative part of the neutral cluster potential surface. Thus the observed bandwidths are cannot be due to dissociation. Rather they must reflect some Franck-Condon profiles for the photo detachment transitions. The dimmer is vibrationally resolved. The loss of vibrational resolution in higher clusters is not surprising in view of the increased number of low frequency vibrational modes in the polyatomic systems. The similarity among the bandwidths suggest that there is a constant offset throughout the copper cluster series between the intensity maxima and the band origin ($v' = 0 \Leftarrow v'' = 0$), whose position determines the adiabatic electron affinity of the neutral molecule. This offset is determined to be 0.05eV for Cu_2^- . Subtraction of this quantity from the vertical electron binding energies of the larger anions yield the adiabatic electron affinities listed in Table I.

Specific clusters: a. Cu_2^- . The spectrum of Cu_2^- is unique among those reported here in displaying the vibrationally resolved structure. An extended portion of the spectrum is shown in FIG.4. The change in the peak spacings from 210 to 265 cm^{-1} at the $\sim 0.84\text{eV}$ peak identifies it as the $v' = 0 \Leftarrow v'' = 0$ transition.

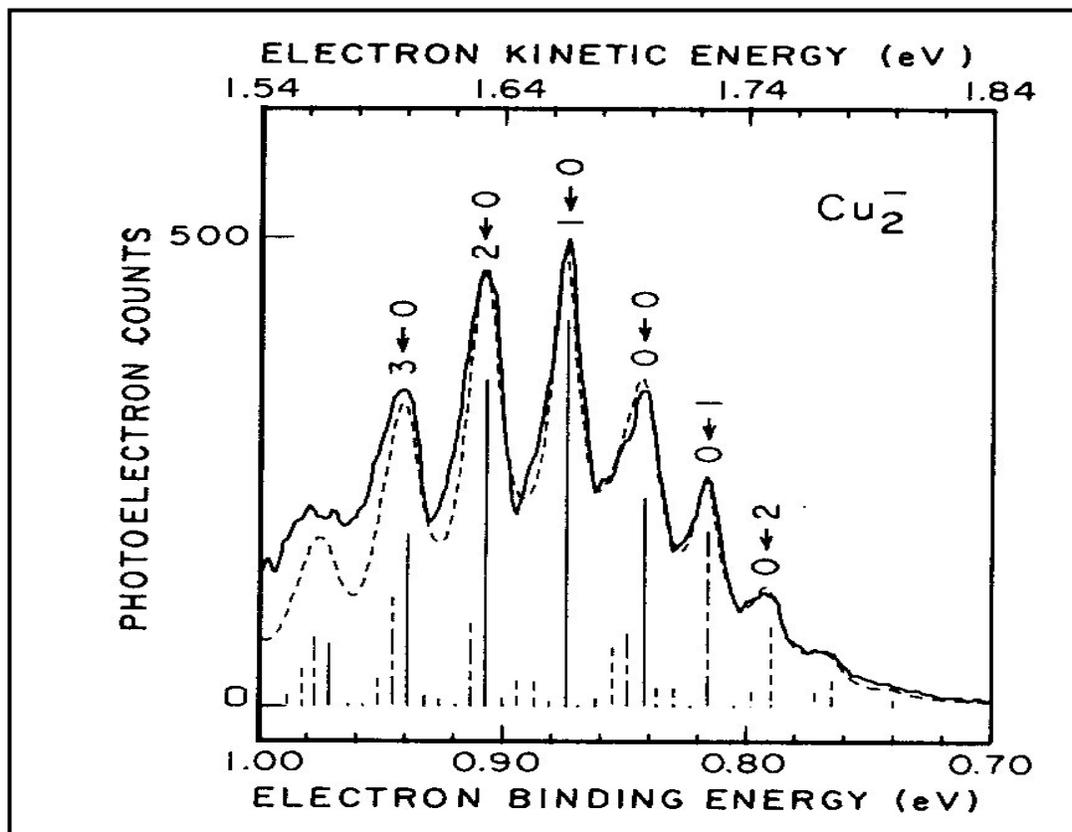


FIG.4. Expanded (488nm) spectrum of Cu_2^- and Franck- Condon simulation (dashed contour). Sticks show transitions from $v'' = 0$ (solid), $v'' = 1$ (long-short dash), and $v'' = 2-4$ in the anion.

This origin band is assigned by a Franck Condon analysis. Using the known vibrational frequency and anharmonicity in the neutral molecule, it was not possible to fit the observed photoelectron spectrum if any other peak were assigned as the origin. Best fits were obtained for an origin band position and thus the adiabatic electron affinity of 0.842eV. Assuming anion anharmonicity is equal to its value in the neutral molecule, the analysis yielded an anion frequency of $210 \pm 15 \text{ cm}^{-1}$, and a bond length difference of $0.125 \pm 0.010 \text{ \AA}$ with respect to the neutral molecule. The values suggest that the addition of extra electron lengthens the bond and the neutral bond length of 2.2197 \AA implies a value of $2.345 \pm 0.010 \text{ \AA}$ for the anion. Calculated Franck Condon factors are illustrated in the FIG. 4 by solid sticks for transitions out of the anion zero point level, and by long-short and short-short dashed sticks for $v'' = 1$ and $v'' > 1$ hot bands, respectively.

The dissociation energy of Cu_2^- can be determined from the adiabatic electron affinities of Cu and Cu_2 and the neutral molecule bond length

($1.96 \pm 0.06 \text{ eV}$) using the relation $D_0(\text{Cu}_2^-) = D_0(\text{Cu}_2) + \text{EA}(\text{Cu}_2) - \text{EA}(\text{Cu})$. The value is found to be $1.57 \pm 0.06 \text{ eV}$, $\sim 20\%$ less than in the neutral molecule. Here despite the formal bond order of 0.5 in Cu_2^- compared to that of 1 in the neutral molecule, the dissociation energy of the neutral molecule is found to be higher compared to that of the neutral molecule which suggests that the extra electron gets extra stabilization due the larger space in the dimer.

b. Cu_3^- . The Cu_3^- spectrum is the only one in which we detect a peak substantially weaker than the main feature. The photo detachment cross section for this weak feature is found to be reduced by a factor of 100. Thus it is highly unlikely to arise from the ground electronic state of Cu_3^- .

Two possible assignments for this peak are to a transition from an electronically excited anion, or from an impurity. Most likely the impurities are metal oxides. The scans at the approximate mass of Cu_3^- (mainly due to Cu_2O_4^-) showed no photo detachment, hence the feature can not be due to metal oxide. Thus the best assignment for the weak band in the Cu_3^- spectrum is to an electronically excited state of the anion. Thus the vertical binding energy, which corresponds to the main feature, is $\sim 2.4 \text{ eV}$. An estimate of the adiabatic electron affinity of Cu_3 is given by the 0.05 eV offset.

The calculations for the equilibrium geometry for the similar systems like Li_3^- , Ag_3^- suggest that the Cu_3^- anion may be linear. Calculations of the neutral Cu_3 potential energy surface predict that the linear structure is $0.2\text{-}0.3 \text{ eV}$ less stable than the Jahn-Teller distorted triangular geometry. Thus the electron affinity may lower by 0.03 eV than the Vertical electron binding energy. It implies that the electron affinity of the Cu_3 molecule would be 2.0 eV .

The dissociation energy of Cu_3^- into Cu^- and Cu_2 can be estimated from the following relation $D_0(\text{Cu}_3^-) = D_0(\text{Cu}_3) + \text{EA}(\text{Cu}_3) - \text{EA}(\text{Cu})$. The value is found to be $2.25 \pm 0.30 \text{ eV}$. Similarly for the process, $\text{Cu}_3^- \rightarrow \text{Cu}_2^- + \text{Cu}$ is determined to be $2.64 \pm 0.30 \text{ eV}$. Thus the trimer bond is much stronger in the anion than the neutral molecule as the neutral Cu_3 the value of $1.08 \pm 0.19 \text{ eV}$.

c. Cu_9^- . It has similar pattern as that of Cu_3^- . Assuming the electron detachment cross section and bandwidth to be similar to that of the series, the vertical electron binding energy between 2.35 and 2.65 eV and an electron affinity between 2.30 and 2.60 eV

4) DISCUSSION:

Electron affinity vs. cluster size:

Experimental results are now available for the copper cluster series enable some general conclusions to be drawn regarding trends in electron affinities as a function of cluster size. Adiabatic electron affinities obtained in the present work for Cu_1 – Cu_2 are illustrated by the solid rectangles in FIG.5.

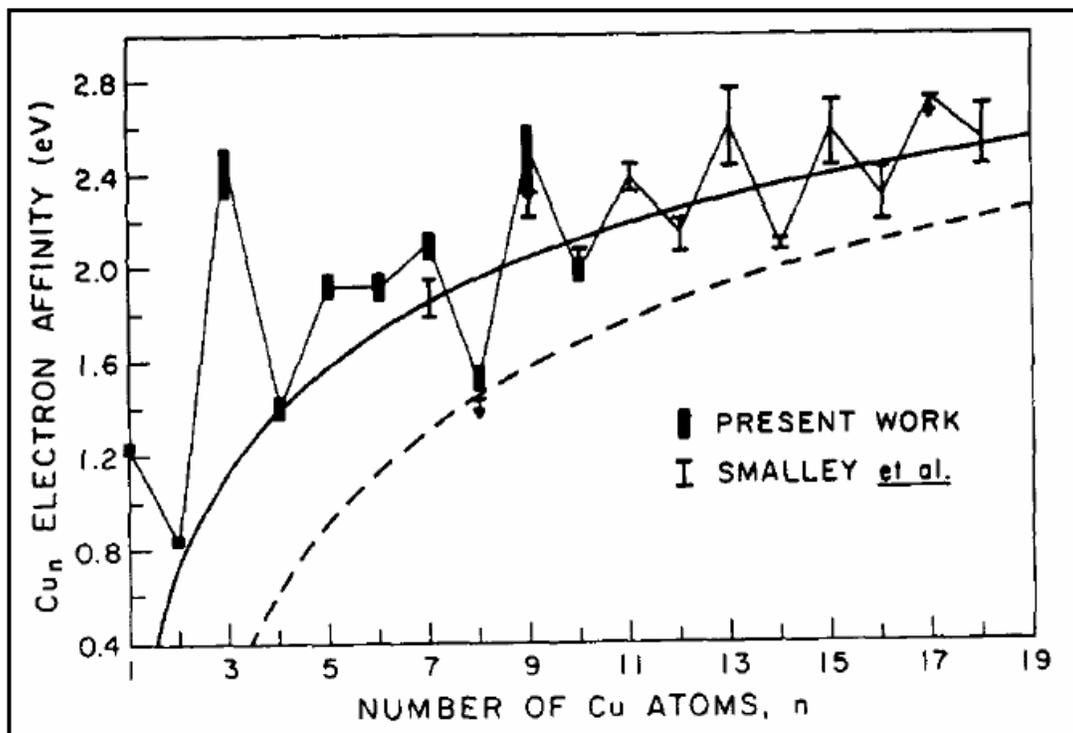


FIG.5. Experimental electron affinities for Cu_n cluster compared with the predictions of the classical spherical drop model. Data for $n=1-10$ are from the present work. The symbol sizes denote the error bars except for the Cu and Cu_2 for which results are more precise than shown. Lines show the electron affinities predicted by $EA=WF-5/8(e^2/R)$, where WF is the work function of the polycrystalline copper and R is the radius of an n atom sphere. The dashed line shows results for $R=n^{(1/3)}r_b$, where $r_b=1.41\text{\AA}$, half the average distance between atoms in the bulk. The solid line is for $R=n^{(1/3)}r_b+\Delta r$, where $\Delta r = a_o(0.53\text{\AA})$.

The heights of these symbols indicate uncertainties in the present measurements, except Cu and Cu₂ for which results are more precise than indicated. Electron affinities recently reported by Smalley and co-workers, from laser-fluence dependence measurements of photoelectron signal intensities, are also in this figure.

These data exhibit two general trends:-

First, there is an over all increase in electron affinities with increasing cluster size.

Second, there is a clear alteration between odd and even cluster sizes, with cluster containing odd numbers of copper atoms having higher electron affinities. This oscillation is particularly pronounced at Cu₃ and Cu₈.

Alternation in photo ionization profile have also been reported for neutral K_n. But ionization potentials of d-shell transition metal clusters such as Nb_n, Fe_n and Ni_n do not alternate.

In contrast to these results, the photo-electron spectra of negatively charged copper clusters display no alternations in peak shape, although alternation in electron affinities are more pronounced. These results imply similar Frank-Condon factors for photo detachment transition from the odd and even copper cluster anions and also suggest that the orbitals associated with the extra electrons in the anions very less in their bonding character than do the HOMO's of the neutral clusters. This inference is consistent with the considerable greater diffuseness of the anion HOMO. The observed electron affinity alternation may be due simply to, screening effects. Since electrons in the same orbital are screened less effectively by each other than by the other closed shell electrons, anions with doubly occupied HOMO's (odd n) will be more stable.

Even / odd alternations in electron affinities and ionization have often been inferred from intensities variations observed in mass spectra which has given earlier. But the intensities generally show a very poor correlation with measured electron affinities. For example, Cu₃ of the highest electron affinities in this series, yet the Cu₃⁻ mass peak relatively weak.

5) SUMMARY:-

The observed results can be summarized as follows:

- 1) Odd>even alternation E.A. with increase in cluster size is superimposed on the overall increase with cluster size with exceptions of same E.A. of Cu₅ and Cu₆ whereas the overall shapes of the photo-electron bands, which reflect F.C. factors for the photo detachment process, are identical for all the cases.
- 2) The photo detachment cross sections of these anions are same within about a factor of 2 and display no even odd alternation.
- 3) Assuming non-degenerate orbitals, the observed alternations in E.A. are consistent with the greater stability of closed shell anions due to screening effects.
- 4) The energies of the excited states of Cu₄⁻, Cu₆⁻, Cu₇⁻, Cu₁₀⁻ decrease with cluster size.
- 5) For Cu₂⁻ the vibration structure in the photo-electron spectrum yields anion bond length, vibrational frequency. The dissociation energy of Cu₂⁻ and Cu₃⁻ are found to be reduced than the neutral molecule
- 6) The Cu₃⁻ displays a weak transition from an electronically excited state of the anion at ~ 0.9eV
- 7) For Cu₈ both E.A and electronic transition energies suggest that the G.S may have special stability.

Comments:

- 1) What is the relevance of comparing the experimental results of vertical binding energy with the classical spherical drop model?

Ans: The calculations for the electron affinity from spherical drop model were compared with the experimental results because this model has been extensively used as model systems for the calculation of the electron affinity. The model was developed by Niels Bohr and Gamow based on some postulates about the nucleus compatible with that of a liquid drop.

A number of energy factors are responsible for binding the nucleons within the nucleus. These are

i) Volume energy (E_v): It is assumed that each nucleon can interact with its nearest neighbor only. E_v = 6AU, where A is the mass number and U is each nucleon-nucleon bond energy. It is often represented as:

$$E_v = a_v A, \text{ where } a_v = 14.1 \text{ MeV}$$

ii) Surface energy: (E_s): The number of nucleons residing on the surface which bind with its neighbors is directly proportional to the surface area. We have:

$4\pi r^2 = 4\pi r_0^2 A^{2/3}$, (as $R = r_0 A^{1/3}$) Therefore the number of surface nucleons experiencing a less binding force compared to the number of nucleons within

the bulk is directly proportional to $A^{2/3}$. Such nucleons reduce the nuclear binding energy. So the surface energy with proper sign is given by:

$$E_s = -a_s A^{2/3}, \text{ where } a_s = 13.0 \text{ MeV}$$

iii) Coulombic energy (E_c): the proton-proton repulsion reduces the nuclear binding energy. E_c is directly proportional to the number of pairs originated from the Z protons, and is given by $Z(Z-1)/2$.

$$E_c = -a_c \{Z(Z-1)\} / A^{1/3}, \text{ where } a_c = 0.60 \text{ MeV}$$

iv.) Asymmetry energy (E_a): We know for heavier elements $N > Z$. Because of the excess neutron region, an asymmetric distribution of the particles with the nucleus appears and it reduces the nuclear binding energy. It is given by:

$$E_a = -a_a (N-Z)^2 A^{-1}, \text{ where } a_a = 19.0 \text{ MeV}$$

v) Pairing energy (E_p): Pairing between the nucleons of the same kind stabilizes the system and it leads to stabilization and similarly the un-pairing leads to destabilization. The pairing energy is given by $E_p = a_p A^{-3/4}$ (for even Z and even N); $= -a_p A^{-3/4}$ (for odd Z and odd N); $= 0$ (for odd A): where $a_p = 34.0 \text{ MeV}$. Therefore the total binding energy is given by:

$$\text{NBE} = E_V + E_S + E_C + E_A + E_P = a_v A - a_s A^{2/3} - a_c \{Z(Z-1)\} / A^{1/3} - a_a (N-Z)^2 A^{-1} + (1; \text{ or } 0; \text{ or } -1) a_p A^{-3/4}$$

2) Why laser light is used in the experiment?

Ans: i) Laser light has high intensity

ii) As the waves in laser light are in phase, the light does not get diffused on passing a long path, hence the photo detachment is obtained more effectively than other conventional source of radiation.

3) Why is the laser beam impinged at the magic angle?

Ans. If the laser beam is directed in magic angle ($54^\circ 45'$), all the anisotropic interactions in the sample will average out to zero, as the $(3\cos^2\theta - 1)$, in the dipolar interaction term will vanish for that the value of $\theta = 54^\circ 45'$.

4) Why negative ion photoelectron spectroscopy for copper clusters is more widely studied than the positive ion photoelectron spectroscopy?

Ans: In negative ion photoelectron spectroscopy, the anion is more stable than the neutral cluster and hence the transitions from the anionic to the neutral molecule can be more effectively studied. Whereas the cationic cluster is less stable than the neutral molecule and the lifetime of these cationic clusters is very short and hence the spectroscopic studies are difficult.

- 5) What kind of detector is used in the study of the photoelectron spectroscopy of copper clusters?

Ans: The electrons that are detached from the anionic clusters by irradiation of laser beam, are focused onto a slit-less entrance of the hemi-spherical electron analyzer, which is usually operated at a transmission energy of 5V. The electrons are accelerated to 300V and are imaged onto the surface of a position sensitive detector. The detector, which is a 2D position sensitive detector, is comprised of a dual micro-channel plate electron multiplier with a 5/8 in. square resistive anode, and it detects single electron events with 0.005 in. resolution ($\sim 2\text{meV}$) and a dead time of $\sim 8\ \mu\text{s}$. The detector output is digitized and stored as a function of the electron energy by a signal averaging data acquisition system.

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