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This chapter summarizes ONR-supported work in Prof. Eyler's laboratories involving small
clusters of As, C, and P, and the coinage metals Ag, Au, and Cu. Charge transfer bracketing
experiments involving cluster ions and neutral molecules of known electron affinities (E.A.) and
ionization potential (I.P.) lead to precise estimates of E.A.'s and I.P.'s for the clusters studied.

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Ion/Molecule Reactions of Metal and Semiconductor Clusters:

Ionization Potentials and Electron Affinities

by

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**Ion/Molecule Reactions of
Metal and Semiconductor Clusters:
Ionization Potentials and Electron Affinities**

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1. Introduction

Among the most important physical properties of small clusters are ionization potentials (IP's) and electron affinities (EA's). These are indicators of both electronic and gross physical structure (if any) possessed by the clusters, and they also serve as one measure of the transition from individual atomic to bulk behavior.¹⁻³ Most experimental determinations of cluster IP's and EA's to date have involved laser photoionization of neutral clusters to produce positive ions⁴⁻⁶ and laser photodetachment of negative cluster ions, sometimes with kinetic energy analysis of the ejected electron.^{2,7,8}

For the past 10 years, our research at the University of Florida has employed Fourier transform ion cyclotron resonance (FTICR) mass spectrometry to study a number of gas phase ionic processes.⁹⁻¹⁴ The FTICR technique¹⁵⁻¹⁸ is perhaps best suited of all mass spectrometric methods for obtaining both qualitative and quantitative information about ion/molecule reactions. Using FTICR ejection capabilities,¹⁹ which impart sufficient kinetic energy to unwanted ions to cause them to strike the analyzer cell plates and be neutralized, ions of all but one mass-to-charge ratio can be removed selectively from the reaction/analyzer cell. Thus complex reaction pathways can be sorted out, and individual reaction rate coefficients can be determined for reactant ions whose energies are very near thermal.²⁰ The variation of rate coefficients with ion kinetic energy (up to 10's of electron volts) can be probed, and the long ion trapping times (many seconds to minutes in duration) permit convenient irradiation with various wavelengths of laser light, if desired.

Experiments carried out in our laboratories²¹⁻²³ have utilized FTICR mass spectrometry to study cluster ions formed directly by laser desorption²⁴ in the FTICR analyzer cell. Since ionization potentials and electron affinities are quite important in understanding cluster properties, and given the power of FTICR to study ionic reactivities, work at the University of Florida has used chemical reactivity of cluster ions, namely their propensity (or lack thereof) to undergo charge transfer reactions, to determine important physical properties of clusters. This chapter summarizes much of the work to date in our laboratories, and also attempts to point out both advantages and disadvantages of the charge transfer bracketing approach. In particular, ionization potentials (IP's) for

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homoatomic clusters of arsenic, As_n ($n = 1 - 5$),²⁵ carbon, C_n ($n = 3 - 32$),^{26,27} phosphorus, P_n ($n = 1 - 4$),²⁵ and small clusters of copper, gold, and silver,²⁸ and electron affinities (EA's) for small and large carbon clusters ($n = 4 - 6, 60, 70$)²⁹ and one silicon cluster (Si_2)²⁹ have been determined by charge transfer bracketing reactions. This technique appears to be applicable to many clusters with IP's $> \text{ca. } 6.5 \text{ eV}$ and/or EA's $< 3.5 \text{ eV}$, and in most cases gives results with uncertainties of $\text{ca. } 0.1 \text{ eV}$. When comparisons can be made, good agreement is almost always found between the IP's and EA's found by this method and well-established experimental and theoretical values. Many IP's have also been measured in this work which have not been determined previously.

Of particular interest in our results is the observation of a periodicity in carbon cluster IP's, with clusters containing $4n + 3$ atoms ($n = 1 - 6$) exhibiting a lower IP than neighboring clusters in the series. Also, our current small carbon cluster electron affinity results suggest EA's for these species substantially below those reported previously from laser photoelectron spectroscopic experiments.^{2,8}

2. Experimental

The experimental methodology employed in these studies has been reported in some detail,^{25,26} and so will only be discussed briefly here, with attention paid to recent modifications of the approach not reported in the earlier literature.

Ions have been formed by direct laser desorption from GaAs (arsenic clusters), graphite (carbon clusters), various foils, alloys, or pressed oxide pellets (coinage metal clusters), and InP (phosphorus clusters) using the focussed output of a pulsed CO_2 or Nd:YAG laser. The laser beam is introduced into the FTICR chamber through a ZnSe (CO_2 laser) or quartz (Nd:YAG laser) window, focussed by a 3 in focal length ZnSe (or quartz) lens through two holes in opposing trapping plates of the FTICR cell, and onto the sample of interest (see Fig. 1). The resultant plume of laser-desorbed ions, neutrals, and electrons enters the FTICR cell, where, depending on the potentials applied to the cell trapping plates, either positive or negative ions are trapped by the combined action of magnetic and static electric fields.

Carbon cluster ions C_n^+ with $n = 6 - 24$ have been produced reproducibly by CO_2 laser irradiation of graphite.²⁶ However, to form smaller ($n = 3 - 5$) and larger ($n = 25 - 32$) positive cluster ions, either the fundamental or the doubled output of a Nd:YAG laser is focussed onto the graphite sample using an internal 3 in (for $n = 3 - 5$ clusters) or an external 1 m focal length quartz lens mounted just outside a quartz window on the FTICR vacuum chamber. Coinage metal clusters, both pure and mixed, are produced using both doubled and tripled Nd:YAG wavelengths. Details of which substrates (and other experimental conditions) lead to the optimum cluster signal are given in ref. 28. Negative carbon cluster ions ($n = 4 - 6$) and Si_2^- are formed from graphite or silicon wafers using either the CO_2 laser as described above or the 532 nm output of the Nd:YAG laser,

focussed using a 3 in focal length quartz lens. C_{60}^- and C_{70}^- are formed by CO_2 laser desorption from an extract of carbon "soot"³⁰ containing appreciable quantities of C_{60} and C_{70} .

All cluster ions but one are next ejected from the FTICR cell using the previously mentioned ejection techniques.¹⁹ A "thermalizing" gas (Ar or SF_6) is then introduced into the vacuum chamber via a pulsed valve, in order to provide a number (> 100) of collisions which relax translational and internal energy of the trapped cluster ions. For work with arsenic, phosphorus, and both smaller and larger carbon cluster ions, the thermalizing gas pressure is allowed to rise into the low to mid 10^{-5} torr range, and is then pumped away rapidly in the next 1 s or so.³¹ Some small As, C, coinage metal, and P cluster ions react with SF_6 , so Ar is used as a thermalizing gas for studies of their charge transfer reactions, even though it is not expected to relax excess internal energy as well as SF_6 .

Next any ions which might form from ion/molecule reactions of the cluster ion of interest during the thermalizing time are ejected from the FTICR cell, leaving only near-thermal cluster ions of a single charge-to-mass ratio in the cell. The ejection of unwanted ions is carried out carefully to avoid imparting excess kinetic energy to the ion of interest during ejection of ions of nearby charge-to-mass ratio.

The charge transfer reaction of the cluster ion of interest with a neutral molecule of known electron affinity or ionization potential (Table I), present at low ($1 - 3 \times 10^{-8}$ torr) pressures in the FTICR cell, is next monitored for a period of time which ranges from 1 to 10 s. The intensity of both the reacting cluster ion and any product ions formed by ion/molecule reactions can be followed conveniently as a function of reaction time. In many cases reactions other than charge transfer are observed. In other (desirable for the purposes of this work) cases, we observe only charge transfer to form the parent ion of the neutral molecule of known ionization potential or electron affinity, or no reaction at all. The ionization potential (or electron affinity) of the cluster species of interest is bracketed between the IP (or EA) of those compounds with which the cluster ion reacts by simple charge transfer, and those with which it does not react.

The neutral molecules of known electron affinity and ionization potential are obtained from commercial sources and used without further purification except for repetitive freeze-pump-thaw cycles. Excitation, detection, and subsequent Fourier transformation of ion signals to obtain mass spectra are carried out using conditions previously reported.^{25,26}

3. Results

3.1 Ionization Potentials. The IP's found²⁵ for small arsenic and phosphorus clusters are given in Table II. As with all of our bracketing experiments, the cluster IP is reported as being halfway between the IP of the compound of lowest IP for which charge transfer (CT) was not observed and the IP of the compound of highest IP for which it was observed. For example, As_3^+ did not undergo charge transfer with *m*-toluidine, but did react via CT with azulene (cf. Table I), bracketing its IP between 7.41 and 7.50 eV. Since the IP of the cluster can actually be anywhere in the gap between the two neutral IP's, uncertainties given in the Tables are generally $\pm 1/2$ the gap size, or ± 0.1 eV when $1/2$ of the gap is smaller than this amount.

The carbon cluster ionization potentials determined in these laboratories^{26,27,33} are given in Table III, again bracketed via CT reactions with the compounds in Table I. An interesting alternation in IP is seen for the carbon clusters, with every fourth cluster having a lower IP than those above or below it. These values have been underlined in the table. Graphical representation of the C_n ionization potential results, which further emphasizes the alternation, is shown in Fig. 2.

Ionization potentials for small coinage metal clusters containing one or two different metals are given in Table IV.²⁸ As with Tables II and III, selected literature values, both experimental and theoretical, are also listed when available.

3.2 Electron affinities. In a manner exactly analogous to the positive ion studies outlined above, charge transfer reactions of negative carbon and silicon cluster ions have been studied. Electron affinity values determined in this manner for $\text{C}_4 - \text{C}_6$, C_{60} , C_{70} , Si and Si_2 are given in Table V. Those for the larger clusters (fullerenes) are in quite good agreement with earlier photoelectron results,⁴⁹ but those for the smaller clusters are substantially below values reported previously.^{2,8,50,52,53}

4. Discussion

It is important to assess the accuracy of the values obtained by any method that purports to determine physical properties, particularly when many of these values have not been reported previously. Comparison with numbers from reliable earlier work is essential in determining whether or not newly-acquired quantities are reliable. Such comparisons are discussed below for both the ionization potential and electron affinity determinations carried out in our laboratories.

4.1 Ionization potentials. Spectroscopic methods have been used previously to determine values for the As and P ionization potentials, and these are thus known to high precision (and, hopefully, accuracy). As can be seen from Table III, carbon cluster IP's have not been measured with any precision prior to this work. The four previously-

reported IP values (for As, P, P_2 , and P_4) judged most reliable by the authors of Ref. 32 are contained within the error limits (two cases) or are no more than 0.1 eV below the lower limits for the IP's determined by the charge transfer bracketing method. This suggests that most translational or internal energy has been removed from even these small cluster ions after the "thermalization" period, with a total residual energy of no more than 0.1 eV above thermal remaining. Similar agreement with well-established IP values is seen for the coinage metal cluster results in Table IV.

The IP's (EA's) of "hot" ions would appear to be higher (lower) than their true values since their excess energy would facilitate charge transfer to a neutral of slightly higher IP (lower EA) than would be the case for completely thermalized ions. Incomplete thermalization might be expected for P_4 , for which the 100 - 300 collisions it can be estimated to make with SF_6 during the thermalization period might not be sufficient to remove all of its internal energy. However, this number of collisions has been shown^{20,54} to thermalize the kinetic energies of ions formed by electron impact in an icr cell, so we would expect better agreement between charge transfer bracketing and spectroscopic results for the As ionization potential. The 0.1 - 0.3 eV discrepancy for As cannot be explained at this time.

Ionization potentials for As_2 through As_5 and for P_3 should be more reliable than earlier determinations (where they exist). In general, these were obtained from electron impact appearance potentials. Thresholds for the appearance of fragment ions formed by electron ionization have generally been found to decrease as improved instrumentation, or the application of photoionization techniques, is used for their determination. Thus our bracketing measurements should provide more reliable IP's, particularly for As_2 and As_4 , where we find values lower than those previously reported.

Accurate experimental IP's for small clusters can be quite useful for testing the quality of new theoretical calculations of cluster properties. The P_4 IP's (and the existence of 2 different P_4^+ isomers) reported in Ref. 25 have already stimulated at least one new theoretical calculation.⁵⁵

An alternation is seen in the carbon cluster IP's (Fig. 2), with clusters having $4n+3$ atoms ($n = 1-6$) exhibiting markedly lower IP's than those of neighboring clusters. It is interesting to note that these cluster sizes are precisely those which have been identified as "magic numbers", possessing special stability.⁵⁶ Most often ion detection after multiphoton ionization is used to identify the relative abundances of neutral clusters. Our work thus suggests that clusters of these sizes **may not possess any special stability**, but rather that they are simply easier to ionize because of their lower IP's.⁵⁷ Because the IP of an atom or molecule is equal to the difference between the energies of the neutral molecule and corresponding positive ion, it is difficult to attribute trends in IP's exclusively to trends in either neutral or ion structures, since both may be involved. However, carbon clusters with $4n+3$ atoms, if they possessed a conjugated π electron system, might give rise to cations with $4n+2$ π electrons which would exhibit enhanced stability (thus leading

to a lower IP for the neutral cluster). If this were the case, and the neutrals also possessed a conjugated π electron system, then carbon clusters with $4n + 2$ atoms (and also this number of π electrons) should be more stable and exhibit higher IP's. Such a trend can also be seen in Table III and Fig. 2, although not as strikingly as the lowered IP's, which are underlined in the Table.

Superimposed on the IP alternation discussed above is a general decrease in ionization potential with increasing n . However, even for $n = 31$ the cluster IP (7.9 ± 0.3 eV) is considerably above the value for bulk graphite of $3.9 - 4.44$ eV,⁵⁸⁻⁵⁹ depending on its form. Ionization potentials have been found³³ to remain in the $6 - 7$ eV range even for clusters of size $C_{50} - C_{200}$, values still much higher than the bulk. This may be due in part to the fullerenic structures of these clusters, dissimilar to the layered structure of bulk graphite.

Our work has reported²⁸ some of the first accurate measurements of the adiabatic ionization potentials of coinage metal clusters larger than the dimer and the first measurements of the adiabatic ionization potentials for any of the mixed clusters studied. In agreement with the predictions of Balasubramanian *et al.*³⁷ and of Flad *et al.*,⁴⁰ we have observed dimer ionization potentials equal within experimental error to those of the atoms, and lower ionization potentials for the trimers and the silver pentamer. Unfortunately, it was not possible to obtain measurements on sufficient species to observe the predicted odd-even alternation in the ionization potential, analogous to that observed in other properties of these species.⁶⁰

Column three of Table IV contains known experimental values of vertical ionization potentials for the coinage metal atoms and clusters. Measurements with the highest degree of accuracy have been limited to the dimers, which, in agreement with our work, have essentially the same ionization potentials as the corresponding atoms. Little insight is provided into the transition from atomic to bulk properties through the intermediate clusters by such limited data. Although our results are less precise than most spectroscopic measurements, the agreement between the values reported here and those derived previously is an important indication of the overall accuracy of the method. Recent electron impact work by Franzreb *et al.*³⁹ is the only other significant experimental determination of ionization potentials. The errors associated with reported ionization potentials in that study were in general larger than those reported here. In spite of this, the agreement with the ionization potentials reported by Franzreb *et al.* is generally good to within their stated error limits.

For the small coinage metal clusters one would expect little difference between vertical and adiabatic ionization potentials, as there should be only minor structural changes between the ion and neutral ground states. The electron transfer we observe, which leads to ionization potential estimates, is not occurring between the ground rovibronic states of the neutral and ion. Due to the low vibrational frequencies of the clusters under study, (e.g. the silver dimer and trimer vibrational frequencies are between

90-200 cm^{-1})⁴⁴ it is obvious that low-lying vibrational states are populated in our ca. 350 K ion/molecule reactions. However, average energies in the ions and neutrals should approximately cancel each other, and any residual error will be small in relation to that due to the separation of the standards in our charge transfer ladder. Thus our results should be quite close to the true adiabatic ionization potentials for the clusters studied, and more accurate than other techniques which can only access vertical ionization potentials.

The theoretical predictions of Balasubramanian et al.,³⁷ Flad et al.,⁴⁰ and the NASA Ames research group^{43,47} are listed in the fourth column of Table IV. Although the theoretical adiabatic ionization potentials are often lower (substantially so for the trimers and pentamers) than the values measured in this work, the overall trends are in agreement. The quantitative differences between theoretical and experimental results are largely due to the difficulties involved in calculating such properties using current *ab initio* methods. The treatment by Flad et al.⁴⁰ predicts a range of values for the adiabatic ionization potential. For a given cluster our experimental ionization potential agrees best with the value predicted for the most stable electronic configuration. There is generally quite good agreement between our results and the "scaled" values calculated by the NASA Ames research group^{43,47} for monomer and dimer IP's. However, more than half of the calculated trimer and pentamer values are at variance with those we have bracketed experimentally. We have no current explanation as to why calculated and experimental IP's agree reasonably well for some of the larger coinage metal clusters, and are in substantial disagreement for others.

4.2 Electron Affinities. The EA's determined by charge transfer bracketing for C_{60} and C_{70} are in quite good agreement with those found by laser photodetachment of negatively charged carbon clusters.⁴⁹ One might expect somewhat lower values from charge transfer bracketing since the photodetachment experiments should determine vertical electron affinities, while charge transfer bracketing gives rise to adiabatic EA's and IP's.^{25,28} This is, in fact, definitely the case for C_4 - C_6 , Si, and Si_2 where Table V shows that values from our laboratories are about 2 eV lower than EA's reported earlier.^{2,50,52,53} A discrepancy this large between vertical and adiabatic EA's is quite unexpected and probably unreasonable. Experiments are underway to investigate possible explanations for the discrepancy, including remaining unrelaxed internal energy in the negative cluster ions, and/or differing structures for ions formed by direct laser desorption vs. in supersonic expansions.²

4.3 Limitations of the Technique. Although reliable IP's and EA's of some species have been determined in a straightforward manner by charge transfer bracketing in the FTICR mass spectrometer, some limitations of the technique should be noted, a few of which have already been mentioned above. 1) Bracketing is either somewhat complicated or not possible at all if reactions other than charge transfer take place between the cluster ion of interest and the neutral molecule. Reactivity of this sort has been seen for a reasonable number of ions and neutral species, particularly the smaller

As, C, and P cluster ions. Of course, these ion/molecule reactions may be of interest in their own right.^{25,28,29} 2) The precision of any bracketing approach will depend on the spacing between the known IP's or EA's of neutral charge transfer agents. Since reactions other than charge transfer can occur, a gap of several tenths of an eV might exist between the IP's or EA's of the two species which react only by charge transfer with the cluster ion, and thus can be used to bracket its IP or EA. 3) The approach can be extended only with difficulty to determination of EA's > ca. 3 eV and/or IP's < ca. 7 eV, due to the lack of suitable reference compounds. The accessible IP range may be lowered closer to 6 eV by some promising di-nitrogen compounds.⁶¹ 4) While large carbon clusters can be produced by direct laser desorption in the FTICR cell, it is difficult to form large cluster ions of many other species in this manner. Supersonic expansion sources are more appropriate for the formation of the larger clusters. The present instrumentation in our laboratories thus limits the cluster sizes whose EA's and IP's we can determine by bracketing. 5) Finally, the question remains as to how close to thermal the ion energies have approached before reacting, with some indication (as discussed above) that 0.1 eV (or more in the case of small negative carbon clusters) translational and/or internal energy remains. The large discrepancies between our EA values for small carbon and silicon ions and those determined previously have yet to be resolved.

5. Conclusions

The IP's of arsenic, carbon, coinage metal, and phosphorus clusters have been determined by charge transfer bracketing in an FTICR mass spectrometer to a precision of a few tenths of an eV. The results are in reasonable agreement with previous reliable experimental IP determinations, and provide the first values necessary to examine the trend of IP's from single atoms to the bulk. They also have served as standards against which to test new theoretical calculations of IP's. The techniques should be useful for studying numerous other small clusters with E.A.'s < ca. 3.0 eV or IP's > ca. 6 eV, whose ions can be produced by direct laser vaporization. Results for carbon clusters indicate that the unusual stability of certain cluster sizes may result solely because of the lower ionization potentials of these clusters.

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Table I
Charge Transfer Compounds Used in Bracketing Experiments

<u>IP³²</u> <u>(eV)</u>	<u>Compound</u>
6.83	N,N-diethyl-p-toluidine
6.93	N,N-dimethyl-p-toluidine
7.00	N,N-diethylaniline
7.13	N,N-dimethylaniline
7.41	azulene
7.50	m-toluidine
7.72	aniline
7.78	phenyl-1,4-benzoquinone
7.80	2-naphthol
7.85	hexamethylbenzene
8.04	durene

Table I, continued

8.13	p-cresol
8.29	m-cresol
8.44	p-xylene
8.56	m-xylene
8.69	p-chlorotoluene
8.82	toluene
8.89	p-dichlorobenzene
9.04	1,2,4-trichlorobenzene
9.11	m-dichlorobenzene
9.18	1,4-difluorobenzene
9.20	fluorobenzene
9.25	benzene
9.30	1,2-difluorobenzene
9.32	tetrachloroethylene
9.35	1,3-difluorobenzene
9.45	2-nitrotoluene
9.48	3-nitrotoluene
9.56	1,4-naphthoquinone
9.88	1-fluoro-3-nitrobenzene
9.91	hexafluorobenzene
10.04	1,4-benzoquinone
10.10	1,2-dicyanobenzene
10.10	1,4-dicyanobenzene
10.23	4-nitrobenzonitrile
10.29	3-nitrobenzonitrile
10.30	1,4-dinitrobenzene
10.43	1,3-dinitrobenzene
10.507	ethylene
10.528	ethylene-d ₄
10.57	hexafluoro-m-xylene
10.7	tetrafluoro-1,4-benzoquinone
11.18	difluoroacetylene
11.394	acetylene
11.4	phosphorous trifluoride
11.77	tetracyanoethylene
12.130	xenon
12.194	acetonitrile
12.32	sulfur dioxide
12.39	freon 13 (CClF ₃)
12.89	nitrous oxide
13.04	sulfuryl fluoride
13.77	carbon dioxide

Table I, continued.

<u>EA³²</u> <u>(eV)</u>	<u>Compound</u>
0.69	azulene
0.86	3-nitro-o-xylene
0.99	3-nitrotoluene
1.10	1,4-dicyanobenzene
1.23	1-fluoro-3-nitrobenzene
1.41	3-nitro- α, α, α -trifluorotoluene
1.56	3-nitrobenzonitrile
1.61	2-nitrobenzonitrile
1.65	1,3-dinitrobenzene
1.72	4-nitrobenzonitrile
1.81	1,4-naphthoquinone
1.91	1,4-benzoquinone
2.00	1,4-dinitrobenzene
2.16	3,5-dinitrobenzonitrile
2.19	2,3-dichloro-1,4-naphthoquinone
2.44	2,5-dichloro-1,4-benzoquinone
2.48	2,6-dichloro-1,4-benzoquinone
2.70	tetrafluoro-1,4-benzoquinone
2.78	tetrachloro-1,4-benzoquinone
3.17	tetracyanoethylene

Table II
As_n and P_n Ionization Potentials Determined
by Charge Transfer Bracketing Reactions

<u>Species</u>	<u>Ionization Potential</u> <u>This work</u>	<u>Literature^a</u>
As	10.00 ± 0.10	9.7883
As ₂	9.89 ± 0.10	(10.1 ± 0.2)
As ₃	7.46 ± 0.10	NA
As ₄	8.63 ± 0.10	(9.07 ± 0.07)
As ₅	7.95 ± 0.10	NA
P	10.50 ± 0.10	10.486
P ₂	10.6 ± 0.1	10.53
P ₃	8.09 ± 0.10	(7.85 ± 0.2)
P ₄	9.28 ± 0.10 ^b	9.08 ± 0.05
	9.23 ± 0.10 ^b	

^a Values in parentheses are those which are "considered not to be firmly established"³² and contain a higher degree of uncertainty.

^b Two isomeric forms of P₄ are present, see Ref. 25.

Table III
C_n Ionization Potentials Determined by Charge Transfer Bracketing

<u>Species</u>	<u>IP / eV (this work)</u>	<u>IP / eV (lit)</u>	
		<u>Expt'l.</u>	<u>Theory</u>
C ₃	13.0 +/- 0.1	(12.3 +/- 0.3) ^a	11.4 ^b
C ₄	12.5 +/- 0.4	(12.6) ^a	10.5
C ₅	12.3 +/- 0.1	9.98 - 12.84 ^c	10.7
C ₆	9.7 +/- 0.2	"	9.8
C ₇	<u>8.1</u> +/- 0.1	"	10.0
C ₈	8.8 +/- 0.1	6.42 - 12.84 ^c	9.2
C ₉	8.8 +/- 0.1	"	9.4
C ₁₀	9.1 +/- 0.1	"	
C ₁₁	<u>7.45</u> +/- 0.1	"	
C ₁₂	8.5 +/- 0.1	"	
C ₁₃	8.1 +/- 0.1	"	
C ₁₄	8.5 +/- 0.1	"	
C ₁₅	<u>7.2</u> +/- 0.1	"	
C ₁₆	8.1 +/- 0.1	"	
C ₁₇	8.1 +/- 0.1	"	
C ₁₈	8.1 +/- 0.1	"	
C ₁₉	<u>7.4</u> +/- 0.1	"	
C ₂₀	8.2 +/- 0.2	"	
C ₂₁	8.2 +/- 0.2	"	
C ₂₂	8.2 +/- 0.2	"	
C ₂₃	<u>7.2</u> +/- 0.3	"	
C ₂₄	7.9 +/- 0.2	"	
C ₂₅	8.0 +/- 0.3	"	
C ₂₆	7.8 +/- 0.1	"	
C ₂₇	<u>7.6</u> +/- 0.1	"	
C ₂₈	7.8 +/- 0.1	"	
C ₂₉	8.1 +/- 0.1	"	
C ₃₀	7.9 +/- 0.2	"	
C ₃₁	<u>7.9</u> +/- 0.3	"	
C ₃₂	<8.04		

Table III, continued

^aGiven in Ref. 32, but stated to be less reliable than other values in the table.^bAll theoretical values from Ref. 34.^cRef. 35.

Table IV

Coinage Metal Cluster Ionization Potentials Determined by Charge Transfer Bracketing

<u>Species</u>	<u>This Work</u>	<u>Literature</u>	
		<u>Experimental</u>	<u>Theoretical</u>
Ag	7.61 ± 0.15	7.58 ³² , 6.4 < IP < 7.947 ³⁶	7.5 ³⁷
Ag ₂	7.61 ± 0.15	7.56 ³⁸ , 6.19 ³⁹ , 6.4 < IP < 7.9 ³⁶ , 7.4 ³²	7.44 ³⁷ , 8.03 ⁴⁰
Ag ₃	7.27 ± 0.15	<7.00 ⁴¹ , 6.45 ± 0.7 ³⁹ , 5.6 < IP < 6.07 ⁴²	5.9 ³⁷ , 5.79 - 7.11 ⁴⁰ 5.6 - 5.8 ⁴³
Ag ₅	<7.00	<7.00 ⁴¹ , 5.6 < IP < 6.4 ³⁶	6.0 - 6.2 ⁴³
Au	9.26 ± 0.10	9.23 ³² , 7.9 < IP ³⁶	9.2 ³⁷
Au ₂	9.16 ± 0.10	9.07 ²² , 9.18 ⁴⁴ , 7.9 < IP ³⁶ , 9.5 ³²	9.4 ³⁷
Au ₃	7.27 ± 0.15	<8.95 ²² , 6.4 < IP < 7.9 ³⁶	6.7 ³⁷ , 7.06 ⁴³
Au ₅	7.61 ± 0.20	6.4 < IP < 7.9 ³⁶	7.46 ⁴³
Cu	7.76 ± 0.10	7.73 ³²	7.84 ⁴³
Cu ₂	7.76 ± 0.10	7.89 ⁴⁵ , 7.46 ± 0.15 ³⁹	8.24 ⁴⁰ , 7.90 ⁴³
Cu ₃	7.07 ± 0.40	6.14 ± 1.0 ³⁹	5.80 - 7.23 ⁴⁰ , 5.79 ⁴³
AgCu	7.61 ± 0.15	7.78 ⁴⁶	7.62 ⁴⁷
Ag ₂ Cu	7.46 ± 0.10		5.72 ⁴⁷
AgCu ₂	7.27 ± 0.15		5.68 ⁴⁷

Table V
C_n and Si_n Electron Affinities Determined by Charge Transfer Bracketing

<u>Species</u>	<u>EA (in eV) (this work)</u>	<u>EA (in eV) (lit)</u>	
		<u>Exp'l.</u>	<u>Theory</u>
C ₄	1.3 +/- 0.1	3.70 ²	3.41 ⁴⁷
C ₅	1.5 +/- 0.1	2.80 ²	2.43 ⁴⁷
C ₆	1.5 +/- 0.1	4.10 ²	3.69 ⁴⁷
C ₆₀	2.6 +/- 0.1	2.6 - 2.8 ⁴⁸	
C ₇₀	2.6 +/- 0.1	2.6 - 2.8 ⁴⁸	
Si	< 0.69	1.385 +/- 0.005 ⁴⁹	1.35 ⁵⁰
Si ₂	0.90 +/- 0.13	2.176 +/- 0.002 ⁵¹ 2.199 +/- 0.012 ⁵²	2.09 ⁵⁰

Figure Captions

Figure 1. Schematic representation of the FTICR analyzer cell and laser focussing arrangement used for cluster ion formation, reactivity studies, and detection.

Figure 2. Graphical representation of C_n (n = 3 - 32) ionization potentials determined in our laboratories.

**ZnSe or Quartz
Focussing
Lens**

**CO₂ or
Nd:YAG**

**Laser
Beam**

**Solids
Probe**

Sample

FTICR Cell



