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Abstract

The ionization potentials of several homoatomic and heteroatomic coinage metal clusters have been determined utilizing charge transfer bracketing and Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. The clusters studied were Ag_n, Au_n, Cu_m, and Ag_kCu_l, where n=2-3,5, m=2,3, and k and l = 1, 2. Atomic ionization potentials were also verified for each of the above metals as a test of the overall bracketing method. This work represents one of the first measurements of adiabatic ionization potentials for any of the above clusters. A number of additional reactions were observed between several of the charge transfer agents and metal cluster ions, including some which resulted in metal-metal bond cleavage.

Introduction

Clusters have been proposed as materials which are intermediate between atoms and bulk solids, and as models of solvation spheres. Their reactivities have been studied as models for surface catalysis, gas plasma and flame chemistry, and processes in interstellar space. Of more practical consideration is the role that progressively smaller metallic and semiconductor structures play in the electronics industry. With the realization that the technology of ultra high resolution microscopy has made it possible to build molecules atom by atom on a surface it becomes increasingly urgent to know the physical properties of such structures. Research into the structure and other properties of these molecules has exploded over the past decade.[1-5] Mass spectrometric and matrix isolation studies have predominated as the main avenues of work and have complemented each other in their attempts to elucidate the structural and electronic properties, as well as the reactivity, of many of these species. However, there remains a paucity of data about many basic physical properties of even the simplest of these molecules. This shortfall not only hinders understanding of these species themselves, but also prohibits a complete interpretation of the reactions which they undergo. It is therefore of primary importance to build a background knowledge of basic physical properties for all of these species.

A number of workers have noted differences in the reactivity of clusters as opposed to the bulk.[6-11] Striking differences in basic physical properties of clusters both as a function of size and in comparison with bulk and atomic properties have been observed.[12-18] This strengthens the view that clusters are indeed a distinct phase of matter with unique physical properties which bear investigation. With this in mind we have attempted to study those properties of clusters which can be suitably investigated utilizing FTICR mass spectrometry.[19-21] This has led to the development of a charge transfer bracketing method for determining ionization potentials, which has been applied to a variety of semiconductor clusters.[15-17] This is the first attempt to apply such a method to metal cluster systems, and the results support the utility of charge transfer bracketing in such systems. This also represents the first such investigation involving bimetallic clusters, a class of clusters which has been given little attention in current research.

Experimental

All work was performed on a home built FTICR mass spectrometer which has been previously described in detail[16] interfaced with a Nicolet[22] FTMS 1000 data station which was equipped with a SWIFT(Stored Waveform Inverse Fourier Transform) module[23]. The cell utilized in all cases was of the dimensions 2.5 x 2.5 x 3.8cm (z-axis). The cell trapping plates (perpendicular to the magnetic field) were machined with one-half inch holes covered with 90% transparent stainless steel mesh to allow passage of the laser beam through the cell and onto the target. The spectrometer utilized a Nicolet prototype superconducting magnet with a 20.3 cm bore and a nominal field strength of 2T. The vacuum system was maintained at $< 5 \times 10^{-9}$ torr utilizing two 10 cm and one 15 cm oil diffusion pumps.[24] Charge transfer agents were introduced into the vacuum chamber at pressures as high as 1×10^{-7} torr above the background by means of a variable leak valve.[25] All clusters were thermalized with argon pulsed into the vacuum chamber with the aid of a solenoid pulsed valve.[26] The transient thermalizing pressure burst reached a maximum value between 1 and 20×10^{-6} torr. Coinage metal samples were introduced into the high vacuum chamber by means of a standard 1m long solids probe and positioned within 1 cm of the trapping plate.

The frequency doubled or tripled output of an Nd-YAG[27] laser was focussed onto the targets by means of a 1 m focal length lens positioned external to the vacuum system. Laser power was in general less than 40mJ per pulse. Samples were composed of various combinations of pure metals, metal oxide mixtures, and arc-melted metal alloys. Metal foils have also been used with some success in past studies by this and other groups to produce small homoatomic metal clusters. Metal oxide mixtures have been used by Freiser et.al. to enhance the production of silver clusters as large as nine atoms.[28] The composition of these pellets was varied from 2:1 to 1:2 in the case of most metal combinations, and up to 4:1 in the case of the Zn:Ag molar ratio; signals strong enough to perform reaction studies were not observed for clusters larger than the pentamer. Mixtures of copper and silver oxides were also used to produce heteroatomic clusters as large as the pentamers Ag_2Cu_3 and Ag_3Cu_2. Mixtures of Au_2O_3 with other metal oxides were also utilized. Difficulties were encountered in compressing the gold oxide to a state which could be desorbed effectively by the laser. All oxide samples were pressed into pellet form using a standard hydraulic press and a modified infrared pellet die which allowed the mixtures to be compressed into a cavity machined in the end of a solids probe tip.

Metal alloys consisting of 50:50 molar mixtures of the three coinage metals were produced utilizing an arc melter, as was one sample composed of a 25:75 mole percent mixture of gold and copper, respectively. This additional copper-gold alloy sample was produced to study the Cu_3Au crystalline phase unique to this alloy. Such samples have been used successfully to produce the CuAu dimer by Morse et. al.[29] Foil and alloy samples were attached to removable probe tips by means of low vapor pressure epoxy. All chemicals used were obtained from Aldrich Inc. and used without further purification.

The pulse sequence utilized in all cases was similar to that previously described.[12] A quench pulse was initially applied to the cell to eject any ions present. After some delay the laser was fired and ions produced. Coincident with this event a pulse valve was triggered to admit thermalizing gas so that the pressure peak would occur shortly after the laser fired, with the delay being optimized to produce the most consistent and strongest signal of the ion of interest. This was followed by a delay for thermalizing of not less than 500ms, after which any unwanted species were then ejected from the cell by either using normal swept frequency ejects or with the capabilities of the SWIFT box. The cluster ion of interest was then allowed to react with the background of charge transfer agent for a variable amount of time after which remaining species were excited and detected.

Results and Discussion

I. Ionization Potentials

Table I shows the bracketed ionization potentials and estimated uncertainties of those metal clusters produced with sufficient intensity to allow study by charge transfer reactions. These include the homoatomic clusters up to the copper trimer, and the silver and gold pentamers, as well as with the mixed metal combinations of copper and silver as large as the trimer. Figure 1 is a spectrum of the mixed metal clusters which could be easily produced using this method. Ionization potentials were not measured for the tetramer species in any case, although all such species were observed. Attempts to react the tetramer clusters with any CTA resulted in loss of the cluster ion signal with no detectable charge transfer in any case. Production of tetramers also proved more troublesome than other species which may indicate adequate production of the species is dependent upon some as yet unknown experimental condition(s). It is also possible that the higher ionization potential expected for this cluster as opposed to either the dimer, trimer, or pentamer would allow for rapid charge transfer and neutralization of these clusters. This possibility was investigated by reducing the time for such reactions to occur within the limits of our instrumentation with little or no improvement in tetramer signal. A more likely possibility is that the production of such cluster species is dependent upon surface conditions which rapidly deteriorate during the ablation process. In support of this, we have observed matrix effects similar to those reported by Freiser et. al.[30] These are manifest in the decay or appearance of a larger ion signal as a function of the number of laser shots impinging upon a single surface position. We have detected the decay of large silver cluster signals after 1-10 lasers shots upon either metal foil or oxide mixture targets. The signal can then be regenerated by moving the laser target to impinge upon a different spot on the target surface. As in the past cases our observation of mass spectra of larger clusters seemed to be enhanced by surface roughening by a varying number of laser shots but the appearance of larger silver and copper clusters was in general short lived. The instability of larger clusters did not extend to the gold clusters. The production of these species was more sensitive to laser power than surface conditions. Gold cluster production could be adjusted from favoring the dimer production to favoring the pentamer by changing the laser power only a few mJ/pulse. Surface roughening and higher laser powers were both found to enhance the production of mixed metal clusters.

The only mixed coinage metal clusters which could be produced in sufficient quantity to enable study were those combinations of copper and silver listed in Table I. Attempts to produce gold-copper and gold-silver combinations were unsuccessful. The attempts to produce laser targets composed of the appropriate metal oxides were unsuccessful due to the difficulties in compressing Au_2O_3 into a satisfactory pellet. The various gold containing alloys were found to produce only atomic species in significant quantities. We have no explanation for this result in light of the success of Morse with similar targets.[29] Contrary to previous results[28] we have also observed the production of mixed metal combinations of silver and zinc from all laser targets composed of their oxides.

This work reports some of the first accurate measurements of the ionization potentials of coinage metal clusters larger than the dimer and the first measurements of the adiabatic ionization potentials for any of the clusters studied. Similar to the study by Smalley et. al.[18] of the electron affinities of small copper clusters, and in line qualitatively with the predictions of Balasubramanian et. al.[31] and of Flad et. al. [32], we have observed an odd even alternation in the ionization potential with a gradual decrease from the atomic value toward the bulk work function of the metals.

Column three of Table I is a listing of known experimental values for vertical ionization potentials for the coinage metal atoms and clusters. Of the clusters only the dimer values and a few of the trimer values have been accurately measured. The clusters for which the ionization potentials have been measured with the highest degree of accuracy are primarily the dimers, which have essentially the same ionization potential as the atom. Such limited information reveals very little of the transition from the atomic to bulk properties through the intermediate clusters. Although our results are less precise than most spectroscopic measurements the agreement between the values reported here and those derived previously is a significant indication of the accuracy of the overall method. The only other significant experimental study of ionization potentials is the recent electron impact work by Franzreb et. al.[33] In that study the errors associated with the reported ionization potentials 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. It should be noted that the values reported here are adiabatic ionization potentials while an electron impact study would yield essentially vertical ionization potentials.

The theoretical predictions of Balasubramanian et. al.[31] and Flad et. al.[32] are listed in column four of Table I. Although the theoretical predictions are substantially lower than ionization potentials measured in this work the qualitative picture of their relative magnitude is preserved in our experimental results. The quantitative disagreement between theoretical and experimental methods is largely due to the difficulties involved in calculating such properties using current ab initio methods. The theoretical treatment by Flad et. al.[32] predicts a range of values for the ionization potential. In this case the best agreement with experimental energies is found for the most stable electronic configuration for each given cluster. However, the disagreement with the well known values for the copper and silver dimers is large and the calculations for the larger clusters are again significantly lower than our values. Qualitatively these calculations again predict the odd-even alternation observed in our experimental results.

The uncertainties for the experimental values derived from this work have been determined by the physical spacing of the ionization potentials of charge transfer agents in our bracketing ladder and uncertainty in the known IP's of the charge transfer agents utilized. The accuracy of the bracketing method is also related to how completely or incompletely the charge transfer agent reacts with the cluster. All of these questions were addressed in the analysis of the absence or presence of a charge transfer reaction. In all cases more than one charge transfer agent was used to determine the occurrence of charge transfer and thus to bracket the ionization potential. The experimental charge transfer results used to obtain the ionization potentials reported in Table I are summarized in Table II as the absence or presence of charge transfer. To accomplish the determination of whether a charge transfer reaction between the cluster under study and the charge transfer agent was occurring it was necessary to evaluate the effect of side reactions on the charge transfer reaction, since such reactions could produce products which could in turn react by charge transfer with the CTA. This was accomplished through a series of studies in which other reaction products were ejected before and during the reaction time to analyze the effect of their presence upon the charge transfer reaction. It was also necessary to set a threshold for the normalized peak intensity of the CTA mass peak which would be interpreted as indicating charge transfer. Our determination was that a CTA peak which was at least 25% of the normalized peak intensity was an indication of the occurrence of charge transfer. Only one borderline case is listed in Table II, that being the reaction between benzene and the gold atomic ion which proceeded at a rate slow enough that the loss of the gold ion signal became significant. This is easily understood since the derived ionization potential for the gold atom is only 0.01 eV larger than the known IP of benzene.

The presence of side reactions in most cases presented a challenge to attaining acceptable results by this method. However, extensive work on the study of side reactions has resulted in narrow bracketing of ionization potentials. This included the use of the FTICR capability of ejecting unwanted product ions as developed by Comisarow. [34] from the cell before and during the reaction study in order to determine the effect, if any, upon the charge transfer products for each of the side-reaction products. In each of these cases the charge transfer product was also ejected before the reaction took place to be certain that no charge transfer from or to unwanted species would occur. After the ejection of all unwanted products the charge transfer reaction was followed for a period of up to several seconds. In the case of each of the bracket defining reactions the charge transfer reaction studied was verified and was found to be the predominant reaction. In several case other side reactions involving metal-metal bond cleavage and adduct formation were observed. In instances where such reactions persisted the relative intensities of peaks were followed as each reaction product was ejected in turn. This was necessary to determine any interference with the charge transfer reaction under study. As discussed previously,[17] the formation of adducts between clusters and charge transfer agents has been thought to occur between species with approximately the same ionization potential by collisional stabilization of the ion/molecule reaction complex.

II. Metal-Metal Bond Cleavage

Perhaps the most interesting of the side reactions occurring in these studies were those few which resulted in metal-metal bond cleavage and destruction of the initial metal cluster species. As can be seen from the listing in Table III, those CTAs which underwent such reactions were primarily aniline derivatives which possess a nitrogen lone pair or which qualify as Lewis bases in some other way. The results of this study have produced a number of additional interactions which may result from the initial adduct formation. A significant acid base interaction has been observed between a number of the charge transfer agents and the 'acidic' metal cluster ions. We attempt here to use the bond cleavages observed in the reactions detailed in Table III in order to fix a lower limit for the metal adduct bond energy based on the well known bond energy of the metal dimers and their cations. This estimate can then be used to extrapolate limits for the bond energies of the larger clusters. The reactions which occur between the CTAs and various metal dimers have been interpreted via the simple thermochemical relation described by Equations 1-3.

$$M_2^+ \;\text{-->}\; M^+ + M \tag{1}$$

$$\underline{M^+ + \text{CTA} \;\text{-->}\; M(\text{CTA})^+} \tag{2}$$

$$M_2^+ + \text{CTA} \;\text{-->}\; M(\text{CTA})^+ + M \tag{3}$$

If an observed reaction is assumed to be exothermic the metal dimer cation bond energy gives a lower limit for the bond dissociation energy of the metal-CTA bond. Although few such energies are experimentally known those which are suggest little difference in the bonding energy of the cation as opposed to the neutral.[31] Where cation bond energies were not available the corresponding neutral dissociation energy has been used to calculate a lower limit for metal-CTA bonds. A listing of the bonding energies derived in this manner is provided in the bottom portion of Table IV.

An examination of Table III reveals that $AgCu^+$ dimer cation reactions with charge transfer agents which were strong Lewis bases resulted in bond cleavage and formation of a copper-CTA complex. In contrast, reaction with the $AgCu_2^+$ trimer cation resulted in the formation of a silver-CTA complex and presumably the Cu_2 neutral. Further, reaction with the Ag_2Cu^+ cluster also results in the formation of a silver-CTA complex. The observed change of products in going from the mixed-metal dimer to the mixed-metal trimers can be related to the bonding strength of the metal dimer which would remain after the reaction of the CTA with the latter.

Table IV lists the bond strengths of several relevant metal dimers. If it is assumed the metal dimer is the most stable leaving group in a reaction between the mixed metal cluster and the CTA, the observed reaction products can be correlated with the metal dimer bond strengths. If the metal CTA bond strength were considerably larger than the bond strength of the remaining dimer then the reaction with the mixed metal trimers would result in a statistical distribution of products based upon the structure of the cluster and to a lesser extent upon the bond strength of the neutral dimer remaining after reaction. Moreover the product distribution would be significantly different for the two trimers studied. Since this is not the case, it must be assumed that the bond strength of the metal dimer neutral which remains after the reaction must be significant with relation to the exothermicity of the overall reaction. Referring to Table IV we see that the bond strengths of the various dimeric combinations of copper and silver follow the trend Ag_2(1.65eV) < AgCu(1.76eV) < Cu_2(2.03eV). Reaction of a CTA with the trimer Ag_2Cu^+ produces only the $Ag(CTA)^+$ product leaving the neutral dimer AgCu which is 0.11eV more strongly bound than the Ag dimer. Of further interest is the reaction of the trimer $AgCu_2^+$ with CTAs which produce only $Ag(CTA)^+$. The latter example again leaves the neutral dimer which is more strongly bound, and in this case a statistical product distribution would oppose the predominance of the observed product. The observed predominance of the more strongly bound neutral leaving group is revealing with regard to the bond dissociation energies of the atom-CTA complex. The sensitivity of reaction products to minute differences in the neutral product bond strength indicates that the atom-CTA bond strength must be on the order of the metal dimer bond strength. This is also a strong indication that the clusters under study have been well thermalized. Assuming that the most stable neutral remaining after the cleavage of the metal-metal bond is either a smaller bare metal cluster or the metal atom the bonding energy of the metal cluster ion may be derived from known thermodynamic quantities.

The reaction products may also be relevant to the proposed structures of the mixed metal trimers. The extraction of a silver atom from both the Ag_2Cu and the Cu_2Ag trimers is interesting in relation to past studies of the structure of these molecules. Howard et. al. [35] have studied the structure of $AgCu_2$ utilizing matrix isolation and ESR spectroscopy and found the molecule to be bent with an acute angle and the silver atom between the two copper atoms. The structure implied by the ESR study above along with those calculated by Walsch et. al.[36] imply that the Cu-Cu bond distance is somewhat less than the Ag-Cu bond distance. This is quite reasonable since it would allow for the possibility of a concerted reaction producing a bond between the two copper atoms as the silver atom was extracted. Comparison of this molecule with similar studies of the silver and copper trimers results in evidence that the $AgCu_2$ cluster has electronic properties closer to the copper trimer than the silver trimer. This is in fact born out by the results of our ionization potential determination since the ionization potential derived for this cluster is somewhat higher than that of Ag_3. The absence of other isomers in the ESR study has been interpreted to mean that the proposed bent structure is a minimum for the molecule. This structure could easily be rationalized in relation to our work. In view of the theoretical treatment of this molecule by Walsch et. al.[36], it is impossible to eliminate any of these structures since they all lie closely enough together in energy to be equally populated under our experimental conditions.

Derived rates for the various reactions resulting in bond cleavage are listed in Table V. Table IV also contains a listing of the metal CTA bond strengths determined by the use of collision induced dissociation (CID)[37]. These were determined as a check of the range of the bond dissociation energies of these complexes indicated by the reactivity of the clusters. The CID results agree favorably with other results in all cases. The recent results of Duncan et al. [38] indicate a value of 2 eV for the upper limit of the silver-benzene bond dissociation energy, quite reasonable compared to our results.

Conclusions

Charge transfer bracketing has proven to be a useful method for determining ionization potentials of highly reactive species such as metal and semiconductor clusters. Variations of the method should be useful for determining other physical properties of these species such as proton and electron affinities. Although direct laser desorption/ionization methods are limited to the production of relatively small cluster ions they are capable of producing large enough quantities of up to five-atom clusters for effective study. Metal oxide mixtures have been utilized to selectively produce high yields of mixed metal clusters by varying the characteristics of the vaporization laser and the oxide mixtures. The ionization potentials determined by the CTA bracketing method agree well with the few well known values for these species, indicating a high degree of accuracy for our method.

The presence of side reactions in addition to charge transfer reactions causes difficulties in the acquisition and interpretation of the charge transfer results. However, detailed study of these reactions may prove useful in studying the dynamics of adsorption onto metal surfaces as it relates to heterogeneous catalysis. The addition of an external ion generation source will make it possible to produce and study larger clusters in the future.

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TABLE I. Ionization Potentials (eV) of coinage metal clusters derived from charge transfer bracketing.

Species	This Work	Literature	
		Experimental	Theoretical
Ag	7.61 ± 0.15	7.56[39], 6.4<IP<7.9[44]	7.5[31]
Ag_2	7.61 ± 0.15	7.56[40], 6.19[33], 6.4<IP<7.9[44]	7.44[31], 8.03[32]
Ag_3	7.27 ± 0.15	<7.00[28], 6.45 ± .7[33], 5.6<IP<6.07[43]	5.9[31], 5.79..7.11[32]
Ag_5	<7.00	<7.00[28], 5.6<IP<6.4[44]	
Au	9.26 ± 0.10	9.22[39], 7.9<IP[44]	9.2[31]
Au_2	9.16 ± 0.10	9.07[41], 9.08[3], 7.9<IP[44]	9.4[31]
Au_3	7.27 ± 0.15	<8.95[41], 6.4<IP<7.9[44]	6.7[31]
Au_5	7.61 ± 0.20	6.4<IP<7.9[44]	
Cu	7.76 ± 0.10	7.72[39]	
Cu_2	7.76 ± 0.10	7.89[3], 7.46 ± .15[33]	8.24[32]
Cu_3	7.07 ± 0.40	6.14 ± 1.0[33]	5.80..7.23[32]
AgCu	7.61 ± 0.15	7.78[42]	
Ag_2Cu	7.46 ± 0.10	NA	
$AgCu_2$	7.27 ± 0.15	NA	

Table II. Bracket defining reactions for all coinage metal clusters studied.

	Cu	Cu_2	Cu_3	Ag	Ag_2	Ag_3	Ag_5	AgCu	$AgCu_2$	Ag_2Cu	Au	Au_2	Au_3	Au_5
Ferrocene			Y											
N,N, Diethyl Toluidine					Y									
N,N. Dimethyl Toluidine			Y		Y	Y		Y						
N,N, Diethyl Aniline			Y		Y	Y	N	Y	Y				Y	
N,N, Dimethyl Aniline			N	Y	Y	Y	N	Y	Y	Y			Y	Y
Azulene		Y	N	Y	Y	N	N	Y	N	Y			N	Y
m-Toluidine	Y	Y		Y	Y	N		Y	N	N			N	Y
Aniline	Y	Y		N	N	N		N	N	N			N	N
2-Napthol	N	N		N	N			N		N				N
Hexamethylbenzene	N	N						N						
p-dichlorobenzene												Y		
1,2,4 Trichlorobenzene												Y		
m-dichlorobenzene											Y	Y		
Fluorobenzene											Y	N		
Benzene											(N)	N		
Tetrachloroethylene											N			

Y = Charge transfer from cluster ion to the chrge transfer agent was observed.

N = No charge transfer observed.

TABLE III. Reactions of charge transfer agents with various metal clusters resulting in bond cleavage or multiple adduct formation.

$AgCu^+$ + Dimethyl Aniline --> Ag + $Cu(DMAN)^+$
$AgCu^+$ + Azulene --> Ag + $Cu(AZ)^+$
$AgCu^+$ + m-Toluidine --> Ag + $Cu(mTol)^+$
$AgCu^+$ + Diethyl Aniline --> Ag + $Cu(DEAN)^+$

Ag_2^+ + DEAN --> Ag + $Ag(DEAN)^+$
Ag_2^+ + DMAN --> Ag + $Ag(DMAN)^+$
Ag_2^+ + mTOL --> Ag + $Ag(mTOL)^+$
Ag_2^+ + Azulene --> Ag + $Ag(AZ)^+$

Au_2^+ + mDichloroBenzene --> Au + $Au(MDCBZ)^+$
Au_2^+ + Benzene --> Au + $Au(BZ)^+$
Au_2^+ + FluoroBenzene --> Au + $Au(FBZ)^+$

$AgCu_2^+$ + DMAN --> $Ag(DMAN)^+$ + Cu_2
$AgCu_2^+$ + DEAN --> $Ag(DEAN)^+$ + Cu_2
$AgCu_2^+$ + mTOL --> $Ag(mTOL)^+$ + Cu_2
$AgCu_2^+$ + AZ --> $Ag(AZ)^+$ + Cu_2

Ag_2Cu^+ + DMAN --> $Ag(DMAN)^+$ + AgCu
Ag_2Cu^+ + mTOL --> $Ag(mTOL)^+$ + AgCu
Ag_2Cu^+ + AZ --> $Ag(AZ)^+$ + AgCu

Cu_2^+ + DMAN --> Cu + $Cu(DMAN)^+$
Cu_2^+ + mTOL --> Cu + $Cu(mTOL)^+$
Cu_2^+ + AZ --> Cu + $Cu(AZ)^+$
Cu_2^+ + AN --> Cu + $Cu(AN)^+$

Table IV. Bond energies(eV) of coinage metal dimers derived from second and third law calculations along with bond strengths of metal-CTA complexes derived from thermochemical relationships and by CID studies.

Species	Exp
Ag_2	1.65[2]
Ag_2^+	1.66 ± .04[31]
AgCu	1.76[2]
Cu_2	2.03[2]
Au_2	2.29[2]
$AgDMAN^+$	1.67 ± .12*
$AgmTOL^+$	1.71 ± .23*
$AgAZ^+$	1.61 ± .27*
$AgDMAN^+$	> 1.66 ~
$AgmTOL^+$	> 1.66 ~
$AgAZ^+$	> 1.66 ~
$AgDEAN^+$	> 1.66 ~
$Au(MDCBZ)^+$	> 2.29 ~
$Au(BZ)^+$	> 2.29 ~
$Au(FBZ)^+$	> 2.29 ~
$CuAZ^+$	> 2.03 ~
$Cu(DMAN)^+$	> 2.03 ~
$Cu(mTOL)^+$	> 2.03 ~
$Cu(AN)^+$	> 2.03 ~

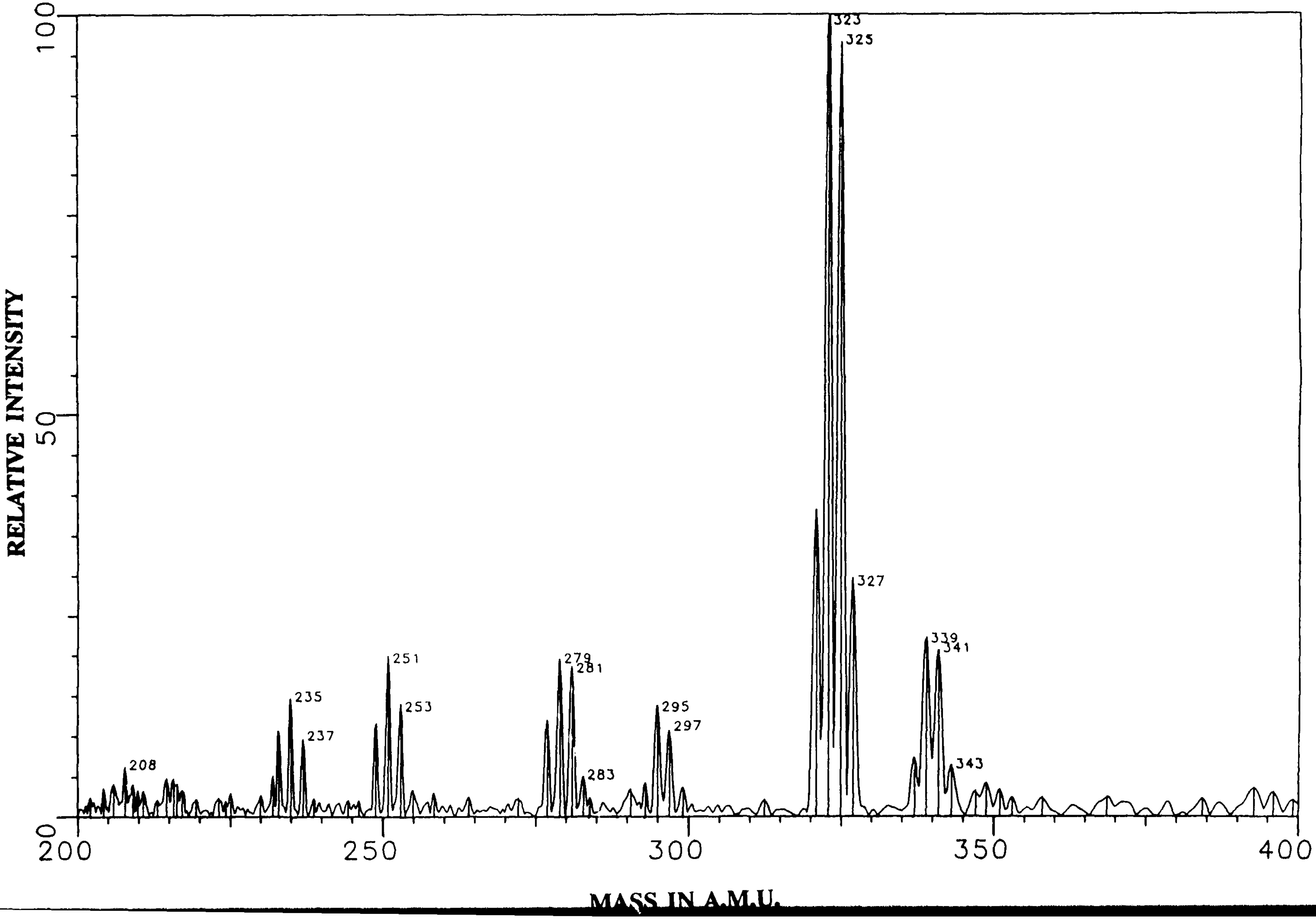
* Determined by CID

~ This work

TABLE V. Reactions rates of charge transfer agents with various metal clusters resulting in bond cleavage. All rates are in units of 10^{-10} cm^3 s^{-1}, and are uncorrected for ion gauge sensitivity.

$AgCu^+$ + Dimethyl Aniline --> Ag + Cu(DMAN)$^+$	4.76 ± .4
$AgCu^+$ + Azulene --> Ag + Cu(AZ)$^+$	4.44 ± .8
$AgCu^+$ + m-Toluidine --> Ag + Cu(mTol)$^+$	0.78 ± .1
$AgCu^+$ + Diethyl Aniline --> Ag + Cu(DEAN)$^+$	5.54 ± .8
Ag_2^+ + DEAN --> Ag + Ag(DEAN)$^+$	0.768 ± .1
Ag_2^+ + DMAN --> Ag + Ag(DMAN)$^+$	0.548 ± .1
Ag_2^+ + mTOL --> Ag + Ag(mTOL)$^+$	0.506 ± .1
Ag_2^+ + AZ --> Ag + Ag(AZ)$^+$	0.618 ± .1
Au_2^+ + mDichloroBenzene --> Au + Au(MDCBZ)$^+$	1.50 ± .1
Au_2^+ + Benzene --> Au + Au(BZ)$^+$	0.72 ± .1
Au_2^+ + FluoroBenzene --> Au + Au(FBZ)$^+$	1.84 ± .3
$AgCu_2^+$ + DMAN --> Ag(DMAN)$^+$ + Cu_2	3.82 ± .1
$AgCu_2^+$ + DEAN --> Ag(DEAN)$^+$ + Cu_2	2.04 ± .3
$AgCu_2^+$ + mTOL --> Ag(mTOL)$^+$ + Cu_2	5.06 ± 1.2
$AgCu_2^+$ + AZ --> Ag(AZ)$^+$ + Cu_2	1.37 ± .3
Ag_2Cu^+ + DMAN --> Ag(DMAN)$^+$ + AgCu	2.42 ± .2
Ag_2Cu^+ + mTOL --> Ag(mTOL)$^+$ + AgCu	2.74 ± .4
Ag_2Cu^+ + AZ --> Ag(AZ)$^+$ + AgCu	6.54 ± .5
Cu_2^+ + DMAN --> Cu + Cu(DMAN)$^+$	2.14 ± .3
Cu_2^+ + mTOL --> Cu + Cu(mTOL)$^+$	0.82 ± .1
Cu_2^+ + AZ --> Cu + Cu(AZ)$^+$	0.96 ± .2
Cu_2^+ + AN --> Cu + Cu(AN)$^+$	1.37 ± .1

Figure I. Larger Copper-Silver Clusters.



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