transfer never occurs in singly linked dimers or heterodimers. For these compounds, exciton coupling or energy transfer is the dominant process.

Another possible way of the singlet excited-state decay via internal conversion is related to the geometry of the dimer and trimer. As suggested earlier,<sup>28</sup> the presence of the basket handle chains, which are semiflexible, might lead to additional vibrational modes which would also enhance the radiationless decay.

#### Conclusion

The systematic study of singly linked and doubly linked face to face porphyrin dimers and trimer allows us to conclude, that, if one takes into account the solvent effect, the molecular exciton theory can be successfully applied to the basket handle compounds, whose exciton interactions are weak. For composite molecules bearing identical chromophores, it clearly appears that there are no charge-transfer states lower than the singlet excited states. The deactivation pathways of the singlet states of the dimer and trimer remain the same as for the monomer, but the decay rates are changed. The radiative (fluorescence) and intersystem crossing rates decrease on behalf of the internal conversion rate. The latter, which is enhanced by a factor of 3 in the doubly linked dimer and trimer, is explained in terms of either the existence of additional vibrational modes due to the presence of the flexible basket handle chains or the existence of virtual transfer states lying near above the singlet ones.

The stabilization effect of the solvent was found to play a crucial role, not only in balancing the exciton coupling energy, but also in lowering the charge-transfer states. We believe that theoretical calculations using either ab initio CI or CNDO/S-CI methods to predict energies of excited and CT states and oscillator strengths would gain in reliability if they could directly include both charge-transfer characters and solvent effect. Such studies are, however, very demanding. They are already underway, but exclusively on small molecules, and should be extended to bigger ones.

# Ionization Potentials and Reactivity of Coinage Metal Clusters

## M. A. Cheeseman and J. R. Eyler\*

Department of Chemistry, University of Florida, Gainesville, Florida 32611-2046 (Received: June 21, 1991; In Final Form: September 24, 1991)

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 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 are currently the focus of several areas of research. It has been proposed that these species represent an intermediate phase between atoms and bulk solids. Studies of cluster reactivities have revealed similarities with and provided insight into such areas as surface catalysis, gas plasma and flame chemistry, and processes in interstellar space. The practical significance of clusters extends to the electronics industry, which is making use of progressively smaller metallic and semiconductor structures. Now that X-ray and electron beam lithography and high-resolution microscopy have made it possible to produce and study nanoscale devices, knowledge of the physical properties of clusters is urgently needed. As a result, research into the structure and other characteristics of these species has exploded over the past decade.<sup>1-5</sup> Mass spectrometric and matrix isolation studies have predominated as the main avenues of work, and they have complemented each other in their attempts to elucidate the structural and electronic properties, as well as the reactivity, of these species. However, there remains a paucity of data about many basic physical properties of even the simplest of clusters. This shortfall hinders the understanding of the species themselves, as well as the complete interpretation of the reactions which they undergo. It is therefore

of primary importance to acquire data on the fundamental physical properties of cluster species.

A number of workers have noted differences in the reactivity of clusters as opposed to that of the bulk.<sup>6-11</sup> Several physical properties have shown distinct variations, both as the size of the cluster changes and in comparison with corresponding values for the bulk and atomic species.<sup>12-18</sup> These observations support the view that clusters do indeed compose a distinct phase of matter with unique properties. For this reason we have attempted to study those properties of clusters which can be suitably investigated by FTICR mass spectrometry.<sup>19-21</sup> This endeavor has led to the

- Ray, U.; Jarrold, M. F. J. Chem. Phys. 1990, 93, 5709
- Č8) Jarrold, M. F.; Ray, U.; Creegan, K. M. J. Chem. Phys. 1990, 93, 224.
- (9) Trevor, D. J.; Cox, D. M.; Kaldor, A. J. Am. Chem. Soc. 1990, 112, 3742 and references therein.
- (10) Hamrick, Y. M.; Morse, M. D. J. Phys. Chem. 1989, 93, 6494 and references therein.

- (11) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne,
  N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups,
  W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl,
  R. F.; Smalley, R. E. J. Phys. Chem. 1990, 94, 8634.
  (12) Parks, E. K.; Klots, T. D.; Riley, S. J. J. Chem. Phys. 1990, 92, 3813.
  (13) Yang, S.; Knickelbein, M. B. J. Chem. Phys. 1990, 93, 1533.
  (14) Vang, B.; Vang, Y. Yang, S.; Bilau, S. J. J. Chem. Phys. 1900, 92

  - (14) Knickelbein, M. B.; Yang, S.; Riley, S. J. J. Chem. Phys. 1990, 93,
- 94.
- (15) Zimmerman, J. A.; Eyler, J. R.; Bach, S. B. H.; McElvany, S. W. J. Chem. Phys. 1991, 94, 3556
- (16) Zimmerman, J. A.; Bach, S. B. H.; Watson, C. H.; Eyler, J. R. J. Phys. Chem. 1991, 95, 98.

0022-3654/92/2096-1082\$03.00/0 © 1992 American Chemical Society

<sup>(1)</sup> Weltner, W., Jr.; Van Zee, R. J. In Proceedings of the Conference on Computational Chemistry: The Challenge of d and f electrons; Salahub, D. R., Zerner, M. C., Eds.; ACS Symposium Series 394; American Chemical (2) Gingerich, K. A.; Brewer, L.; Winn, J. S.; Miedema, A. R.; Ozin, J.

Faraday Symp. Chem. Soc. 1980, 14 and references therein.

<sup>(3)</sup> Morse, M. D. Chem. Rev. 1986, 86, 1049 and references therein. (4) Russell, D. H., Ed. Gas Phase Inorganic Chemistry; Plenum Publishing: New York, 1989 (and references therein).

<sup>(5)</sup> Weltner, W., Jr.; Van Zee, R. J. Chem. Rev. 1989, 89, 1713.

<sup>(6)</sup> Davis, S. C.; Klabunde, K. J. Chem. Rev. 1982, 82, 153.

<sup>(17)</sup> Bach, S. B. H.; Eyler, J. R. J. Chem. Phys. 1990, 92, 358.
(18) Pettiette, C. L.; Yang, S. H.; Craycroft, M. J.; Conceicao, J.; Laaksonen, R. T.; Cheshnovsky, O.; Smalley, R. E. J. Chem. Phys. 1988, 8, 5377.
(19) Buchanan, M. V.; Comisarow, M. B. In Fourier Transform Mass

Spectrometry: Evolution, Innovation, and Applications; Buchanan, M. V., Ed.; ACS Symposium Series 359; American Chemical Society: Washington, DC, 1987, p 1.

#### IPs and Reactivity of Coinage Metal Clusters

development of a charge-transfer bracketing method for the determination of cluster adiabatic ionization potentials. Although the procedure has been applied to a variety of semiconductor clusters,<sup>15-17</sup> this is our first attempt to extend the approach to metal cluster systems. This paper describes the successful extension of charge-transfer bracketing to clusters of the Cu, Ag, and Au group, and also represents the first results of this type for bimetallic systems, a class of clusters which has received little attention.

#### **Experimental Section**

All work was performed on a home-built FTICR mass spectrometer, which has been previously described in detail,<sup>16</sup> and which is interfaced with a Nicolet<sup>22</sup> FTMS 1000 data station equipped with a SWIFT (stored waveform inverse Fourier transform) module.<sup>23</sup> The cell utilized in all cases was of the dimensions  $2.5 \times 2.5 \times 3.8$  cm (z axis). The cell trapping plates (perpendicular to the magnetic field) were machined with 1.25cm-diameter 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 2 T. The vacuum system was maintained at  $<5 \times$ 10<sup>-9</sup> Torr by two 10-cm and one 15-cm oil diffusion pumps.<sup>24</sup> Charge-transfer agents (CTAs) were introduced into the vacuum chamber at pressures as high as  $1 \times 10^{-7}$  Torr above the background by means of a variable leak valve.<sup>25</sup> All clusters were thermalized with argon pulsed into the vacuum chamber with the aid of a solenoid pulsed valve.<sup>26</sup> The thermalizing argon pressure reached a maximum value between 1 and  $20 \times 10^{-6}$  Torr. Coinage metal samples were introduced into the high-vacuum chamber by means of a standard 1-m-long solids probe and were positioned within 1 cm of the cell trapping plate. The frequency-doubled or -tripled output of a Nd:YAG<sup>27</sup> laser was focused onto the targets by means of a 1-m focal length lens positioned external to the vacuum system. Laser energy incident upon the samples was in general less than 40 mJ per pulse with a spot size less than 2 mm in diameter.

The pulse sequence utilized in all cases was similar to that previously described.<sup>16</sup> A quench pulse was initially applied to the cell to eject any ions present. After some delay, the laser was fired and ions were 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 thermalization period of not less than 500 ms, after which any unwanted species were removed from the cell using either normal swept frequency ejection or the capabilities of the SWIFT technique. The cluster ion of interest was then allowed to react with the background of the charge-transfer agent for a variable amount of time after which remaining species were excited and detected.

Collision-induced dissociation (CID) was used to determine the bond strength of several silver-CTA complexes. The experimental sequence employed was similar to that described earlier.<sup>28</sup> Complexes were isolated and allowed to undergo collisional relaxation with the background pressure of argon for 500 ms. A brief radio frequency excitation was then used to impart a known

TABLE I: Ionization Potentials (eV) of Coinage Metal Clusters Derived from Charge-Transfer Bracketing. Uncertainties Are Given as 95% Confidence Intervals

		literature					
species	this work	experimental	theoretical				
Ag	$7.61 \pm 0.15$	$7.58^{43}_{,43} 6.4 < IP < 7.9^{47}_{,58}$	7.531				
Ag <sub>2</sub>	$7.61 \pm 0.15$	$7.56^{45}, 6.19^{35}, 6.4 < IP < 7.9^{47}, 7.4^{43}$	7.44, <sup>31</sup> 8.03 <sup>34</sup>				
Ag <sub>3</sub>	$7.27 \pm 0.15$	$<7.00^{29}, 6.45 \pm 0.7^{35}, 5.6 <$ IP < $6.07^{46}$	5.9, <sup>31</sup> 5.79-7.11 <sup>34</sup>				
Ag	<7.00	$<7.00^{29}$ 5.6 $<$ IP $<$ 6.4 <sup>47</sup>					
Au	$9.26 \pm 0.10$	$9.23^{43}$ 7.9 < IP <sup>47</sup>	9.2 <sup>31</sup>				
Au <sub>2</sub>	9.16 ± 0.10	$9.07,^{44}, 9.18,^{33}, 7.9 < IP,^{47}$ $9.5^{43}$	9.4 <sup>31</sup>				
Au₁	$7.27 \pm 0.15$	<8.95, <sup>44</sup> 6.4 < IP < 7.9 <sup>47</sup>	6.7 <sup>31</sup>				
Au	$7.61 \pm 0.20$	$6.4 < IP < 7.9^{47}$					
Cu	$7.76 \pm 0.10$	7.73 <sup>43</sup>					
Cu <sub>2</sub>	$7.76 \pm 0.10$	$7.89.^{48}$ 7.46 ± 0.15 <sup>35</sup>	8.24 <sup>34</sup>				
Cu	$7.07 \pm 0.40$	$6.14 \pm 1.0^{35}$	5.80-7.23 <sup>34</sup>				
AgCu	$7.61 \pm 0.15$	7.78 <sup>38</sup>					
Ag <sub>2</sub> Cu	$7.46 \pm 0.10$	NA					
AgCu <sub>2</sub>	7.27 ± 0.15	NA					

kinetic energy to the ion. The products of the collisions of the excited ions and the background gas were then followed to determine the extent of dissociation. By calculation of the center-of-mass kinetic energy for the Ar/(silver-CTA)<sup>+</sup> collision encounter, it was possible to extrapolate values for the bond strengths of these complexes.<sup>28</sup>

Laser targets were composed of various combinations of pure metal foils, arc-melted metal alloys, and mixtures of metal oxides. Homoatomic gold and copper clusters investigated here were produced by direct laser desorption from metal foil targets. Three metal alloys, each consisting of equimolar mixtures of two of the three coinage metals, were fused with an arc melter, as was one sample composed of a 25:75 mol % Au-Cu mixture. This additional copper-gold sample was produced to determine if unique clustering could be observed for the Cu<sub>3</sub>Au crystalline phase of this alloy. Foil and alloy samples were attached to removable probe tips by means of low vapor pressure epoxy.

Mixtures of silver and zinc oxides have been used by Freiser et al. to enhance the production of silver clusters as large as nine atoms,<sup>29</sup> and similar mixtures were used to produce the silver species studied here. Mixtures of copper and silver oxides were also used to produce heteroatomic cluster ions as large as the pentamers  $Ag_2Cu_3^+$  and  $Ag_3Cu_2^+$ . The composition of the oxide pellets was varied from 2:1 to 1:2 (metal:metal mole ratio) in the case of most metal combinations and up to 4:1 in the case of the Zn:Ag molar ratio. Mixtures of Au<sub>2</sub>O<sub>3</sub> with other metal oxides were also utilized. 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. However, difficulties were encountered in compressing the gold oxide to a state which could be desorbed effectively by the laser. All chemicals used were obtained commercially<sup>30</sup> and used without further purification, except for removal of dissolved gases by multiple freezepump-thaw cycles.

#### **Results and Discussion**

I. Ionization Potentials. Table I shows the bracketed adiabatic ionization potentials and estimated uncertainties obtained in this work for 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 the mixed-metal combinations of copper and silver as large as the trimer. Ionization potentials were not measured for any of the tetramer species, although all such species

<sup>(20)</sup> Baykut, G.; Eyler, J. R. TrAC, Trends Anal. Chem. (Pers. Ed.) 1986, 5, 44.

<sup>(21)</sup> Marshall, A. G.; Grosshans, P. B. Anal. Chem. 1991, 63, 215A.
(22) Now sold by Extrel, P.O. Box 4508, Madison, WI 53711.
(23) Marshall, A. G.; Wang, T.-C.; Ricca, T. L. J. Am. Chem. Soc. 1985.

<sup>107, 7893.</sup> Sold under license from Extrel by T. L. Ricca Associates, 1413

Wyandotte Rd., Columbus, OH 43212. (24) Alcatel Vacuum Products, 40 Pondpark Road, Hingham, MA 02043. (25) Varian Model 951-5100 variable leak valve, Varian Vacuum Products,
 121 Hartwell Ave., Lexington, MA 02173.

<sup>(26)</sup> General Valve Corp. Model 9-181-900, 202 Fairfield Rd., P.O. Box 1333, Fairfield, NJ 07006

<sup>(27)</sup> Continuum Model 581C Nd:YAG laser, Continuum Corporation,

 <sup>(28)</sup> Katritzky, A. R.; Watson, C. H.; Dega-Szafran, Z.; Eyler, J. R. J. Am. Chem. Soc. 1990, 112, 2471.

<sup>(29)</sup> Buckner, S. W.; Gord, J. R.; Freiser, B. S. J. Chem. Phys. 1988, 88, 3678.

<sup>(30)</sup> All chemicals may be obtained from the Aldrich Chemical Co., Milwaukee, WI 53233.



Figure 1. Clusters produced from a target composed of copper and silver oxides with a 50:50 Cu:Ag mole ratio.

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 the formation of the other clusters, an indication that adequate production of the tetramers is dependent upon some as yet unknown experimental condition(s).

It is also possible that the higher ionization potential expected<sup>31</sup> for the tetramer, as opposed to that of either the trimer or pentamer, would lead to rapid charge transfer and neutralization of this size cluster. 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 the tetramer signal. A more likely explanation 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.<sup>32</sup> These are manifest by the initial appearance of a larger cluster ion signal after a few laser shots, followed by the gradual decay of the signal as additional laser shots change the surface. We have detected the decay of signals from silver and copper cluster ions larger than the trimer after 1-10 laser shots on either metal foil or oxide mixture targets. The signal was regenerated by moving the laser target to expose a fresh surface.

In contrast, no such problems were encountered in the production of gold pentamer cluster ions. The formation of gold cluster ions was found to be more sensitive to laser power than to surface conditions. Gold cluster ion production could be adjusted from favoring the dimer to favoring the pentamer by changing the laser power only a few mJ per pulse. Surface roughening and higher laser powers were both found to enhance the production of mixed-metal cluster ions. Again, neither the gold nor the mixed-metal systems produced significant amounts of tetramers.

The only mixed coinage metal cluster ions which could be generated in sufficient quantity to enable study were the 1:1, 1:2, and 2:1 combinations of copper and silver. Figure 1 shows a variety of mixed Ag-Cu cluster ions which could be produced easily by laser desorption from the mixed-oxide targets. Attempts to produce gold-copper and gold-silver combinations were unsuccessful. Targets composed of the appropriate metal oxides could not be used because of difficulties in compressing Au<sub>2</sub>O<sub>3</sub> into a satisfactory pellet, and gold-containing alloys were found to produce only atomic species in significant quantities. In light of the success of Morse with alloy targets,<sup>33</sup> there is no obvious explanation for our results. As mentioned above, the formation of clusters is often highly dependent on the exact experimental conditions, and contrary to previous results,<sup>29</sup> we have observed mixed-metal clusters of silver and zinc from all laser targets composed of their oxides.

This work reports 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 clusters studied. In agreement with the predictions of Balasubramanian et al.<sup>31</sup> and of Flad et al.,<sup>34</sup> 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.18

Column three of Table I 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 this work, have essentially the same ionization potentials as the corresponding atoms. Such limited data provide little insight into the transition from 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 an important indication of the overall accuracy of the method. The only other significant experimental determination of ionization potentials is the recent electron impact work by Franzreb et al.<sup>35</sup> 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 electron impact and other studies have

 <sup>(31)</sup> Balasubramanian, K.; Feng, P. Y. Chem. Phys. Lett. 1989, 159, 452.
 (32) Gord, J. R.; Buckner, S. W.; Freiser, B. S. Chem. Phys. Lett. 1988, 153, 577.

 <sup>(33)</sup> Bishea, G. A.; Morse, M. D. Chem. Phys. Lett. 1990, 171, 430.
 (34) Flad, J.; Igel-Mann, G.; Preuss, H.; Stoll, H. Surf. Sci. 1985, 156, 379; J. Chem. Phys. 1984, 90, 25.

<sup>(35)</sup> Franzreb, K.; Wucher, A.; Oechsner, H. Z. Phys. At., Mol. Clusters 1990, 17, 51.

charge-transfer agent	IP, eVª	Cu	Cu <sub>2</sub>	Cu <sub>3</sub>	Ag	Ag <sub>2</sub>	Ag <sub>3</sub>	Ag <sub>5</sub>	AgCu	AgCu <sub>2</sub>	Ag <sub>2</sub> Cu	Au	Au <sub>2</sub>	Au <sub>3</sub>	Au <sub>5</sub>
ferrocene	6.75			Y											
N,N-diethyl-p-toluidine	6.83				Y										
N,N-dimethyl-p-toluidine	6.93			Y		Y	Y		Y						
N,N-diethylaniline	7.00			(Y)		Y	Y	N	Y	Y				Y	
N,N-dimethylaniline	7.13			(N)	Y	Y	Y	Ν	Y	Y	Y			Y	Y
azulene	7.41		Y	N	Y	Y	Ν	Ν	Y	N	Y			Ν	Y
<i>m</i> -toluidine	7.50	Y	Y		Y	Y	Ν		Y	Ν	Ν			Ν	Y
aniline	7.72	Y	Y		Ν	Ν	Ν		Ν	N	N			N	(N)
2-naphthol	7.80	Ν	Ν		Ν	Ν			N		Ν				Ň
hexamethylbenzene	7.85	Ν	Ν						Ν						
<i>p</i> -dichlorobenzene	8.89												Y		
1.2.4-trichlorobenzene	9.04												Y		
m-dichlorobenzene	9.11											Y	Y		
fluorobenzene	9.20											Y	Ν		
benzene	9.25											(N)	Ν		
tetrachloroethylene	9.32											Ň	-		

<sup>a</sup>Ref. 43, uncertainties are generally  $\leq 0.05$ . Y = charge transfer from cluster ion to the charge-transfer agent was observed. N = no charge transfer observed. () = borderline cases (see text for discussion).

yielded vertical ionization potentials. Adiabatic ionization potentials are measured between the ground rovibronic state of the neutral and that of the ion. Thus any energy change due to structural rearrangement upon ionization is included. Conversely, the vertical ionization potential relates to the energy difference between the ground state of the neutral and the lowest accessible state of the ion with the same internuclear distances as in the neutral. The difference between these two ionization potential measures will only be great if there is significant structural rearrangement in the ion ground state as compared with the neutral.

For the cluster species studied here, we expect little difference between vertical and adiabatic ionization potentials, as there should be only minor structural changes between the ion and the 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 and 200 cm<sup>-1</sup>)<sup>33</sup> 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.<sup>31</sup> and Flad et al.<sup>34</sup> are listed in column four of Table I. Although the theoretical adiabatic ionization potentials are often lower (substantially so for the trimers) 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.<sup>34</sup> predicts a range of values for the adiabatic ionization potential. For each given cluster, the experimental ionization potential agrees best with the value predicted for the most stable electronic configuration. However, these theoretical results show a large disagreement with the well-known values for the larger clusters are consistently lower than our results.

As in previous studies,<sup>15–17</sup> uncertainties in the ionization potentials (IPs) reported here have been determined by the numerical spacing of the ionization potentials of charge-transfer agents in the bracketing ladder and the uncertainty in the known IPs of the charge-transfer agents themselves. The accuracy of the braketing method is also related to how completely the chargetransfer agent reacts with the cluster. In all cases, more than one charge-transfer agent was used to determine the occurrence or absence 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.

The presence of side reactions in most cases presented a challenge to attaining acceptable results by this method. However, extensive study of side reactions has resulted in a better understanding of the overall chemistry of these systems and thus in narrow bracketing of ionization potentials. In all studies, any reaction product formed during the thermalization period was ejected<sup>36</sup> before the subsequent reaction period took place to be certain that no charge transfer from or to unwanted species would occur. In the case of each of the bracket-defining reactions, the charge-transfer reaction studied was followed for as long as several seconds and was found to be the predominant reaction. In several cases, 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, to determine if there was any interference with the charge-transfer reaction under study. The formation of adducts between clusters and charge-transfer agents was thought to involve species with approximately the same ionization potential,<sup>17</sup> as a result of collisional stabilization of the ion/molecule reaction complex. The presence of side reactions such as those discussed above is an indication that more complex interactions may very likely be taking place.

To determine the presence of charge transfer, it was also necessary to set a threshold for the normalized intensity of the CTA mass peak which was indicative of reaction. Our determination was that an intensity for the CTA peak which exceeded 25% of the normalized intensity of the cluster under study was an indication of the occurrence of charge transfer. Only a few borderline cases were encountered, and all are listed in Table II. These cases are in general due to the charge-transfer reaction being sufficiently slow that loss of the cluster ion signal became significant. Such slow reactivity may be related directly to the propinquity of the ionization potentials of the charge-transfer agents and the clusters and may reflect a fundamental limitation of the method.

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. The bond cleavage observed in the reactions detailed in Table III can be used to fix a lower limit for the metal-adduct bond energy based on the well-known bond energies of the metal dimers and their cations.

The reactions which occur between the CTAs and the various metal dimers can be interpreted via the simple thermochemical relation described by eqs 1-3, where  $\Delta H_{BE}$  is the dissociation

<sup>(36)</sup> Comisarow, M. B.; Grassi, V.; Parisod, G. Chem. Phys. Lett. 1978, 57, 413.

$$M_2^+ \rightarrow M^+ + M \quad \Delta H_{BE1}$$
 (1)

$$M^+ + CTA \rightarrow M(CTA)^+ -\Delta H_{RE}$$
 (2)

net: 
$$M_2^+ + CTA \rightarrow M(CTA)^+ + M \quad \Delta H = \Delta H_{BE1} - \Delta H_{BE2}$$
 (3)

enthalpy of the bond in the corresponding reaction. If an observed reaction of the type represented by eq 3 is assumed to be exothermic, the metal dimer cation bond energy gives a lower limit for the bond dissociation energy of the metal–(CTA) cation bond. The metal dimer cation bond energies have been determined thermochemically using the known bond energy of the neutral species and the ionization potentials determined in this work. The results are given in Table IV with values determined experimentally using similar methods<sup>3,37,38</sup> and theoretical predictions.<sup>31</sup> These results indicate that there is little difference between the ion bond energies and the neutral bond energies. Table IV also includes a listing of the bond energy limits for metal–(CTA)<sup>+</sup> ions derived by thermochemical analysis.

The results presented in Table III show that bond cleavage reactions of AgCu<sup>+</sup> result in the formation of the Cu-(CTA) cation while the mixed trimers AgCu<sub>2</sub><sup>+</sup> and Ag<sub>2</sub>Cu<sup>+</sup> cleave to form  $Ag-(CTA)^+$ . The observed change of products in going from the mixed-metal dimer to the mixed-metal trimers must be related to the bond strength of the metal dimer produced as a result of the trimer-(CTA) reaction. Table IV lists the bond strengths of several relevant metal dimers and dimer cations. The most reasonable explanation for the preponderance of one channel for the trimer-(CTA) reactions is that the overall reactions must be close to thermoneutral and therefore very sensitive to the bond energy of the remaining neutral dimer. Although it cannot be shown quantitatively from the data obtained in this work, the implication of near thermoneutrality for the reactions discussed above is that the metal-(CTA) bond strength does not vary greatly from that of the metal-metal bond strength in the clusters under study. A markedly different bond energy for the metal-(CTA) species would logically lead to either no reaction or a statistical distribution of products based upon the structure of the cluster and to a much lesser extent upon the bond strength of the neutral dimer remaining after reaction. Moreover, in the latter case, the product distribution would be significantly different for the two trimers studied. The observation of singular products for these reactions is an indication that the cluster ion-(CTA) complex is a long-lived one which produces the most stable products. This is also a strong indication that the ionization potentials reported here are indeed adiabatic and that the clusters under study were well thermalized.

The extraction of a silver atom from both  $Ag_2Cu^+$  and  $Cu_2Ag^+$ is interesting in relation to past studies of the structure of the corresponding neutral molecules. Howard et al.<sup>39</sup> studied the structure of AgCu<sub>2</sub> utilizing matrix isolation and ESR spectroscopy and found the molecule to be bent with an acute angle and the silver atom at the vertex. In the structure determined by the ESR study, as well as that calculated by Walsch et al.,40 the Cu-Cu distance is somewhat less than the Ag-Cu bond distance. If there is little change between the neutral and corresponding ion structures, this is quite reasonable in light of our results, 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 by the CTA. The absence of other isomers in the ESR study<sup>39</sup> has been interpreted to mean that the proposed bent structure is a minimum for the molecule. However, results of the theoretical treatment of this molecule by Walsch et al.<sup>40</sup> suggest that a number of possible structures lie close in energy.

Table IV also gives values of metal-CTA bond strengths determined by threshold CID measurement, which were measured

TABLE III: Reactions of Charge-Transfer Agents and Various Metal Clusters Resulting in Metal-Metal Bond Cleavage<sup>a</sup>

```
AgCu<sup>+</sup> + DMAN → Ag + Cu(DMAN)<sup>+</sup>

AgCu<sup>+</sup> + AZ → Ag + Cu(AZ)<sup>+</sup>

AgCu<sup>+</sup> + m-TOL → Ag + Cu(m-TOL)<sup>+</sup>

AgCu<sup>+</sup> + DEAN → Ag + Cu(DEAN)<sup>+</sup>

Ag<sub>2</sub><sup>+</sup> + DEAN → Ag + Ag(DEAN)<sup>+</sup>

Ag<sub>2</sub><sup>+</sup> + DMAN → Ag + Ag(DMAN)<sup>+</sup>

Ag<sub>2</sub><sup>+</sup> + m-TOL → Ag + Ag(m-TOL)<sup>+</sup>

Ag<sub>2</sub><sup>+</sup> + AZ → Ag + Ag(AZ)<sup>+</sup>

Au<sub>2</sub><sup>+</sup> + m-DCBN → Au + Au(m-DCBZ)<sup>+</sup>

Au<sub>2</sub><sup>+</sup> + BN → Au + Au(BZ)<sup>+</sup>

Au<sub>2</sub><sup>+</sup> + FBZ → Au + Au(FBZ)<sup>+</sup>

AgCu<sub>2</sub><sup>+</sup> + DMAN → Ag(DMAN)<sup>+</sup> + Cu<sub>2</sub>

AgCu<sub>2</sub><sup>+</sup> + DEAN → Ag(DEAN)<sup>+</sup> + Cu<sub>2</sub>

AgCu<sub>2</sub><sup>+</sup> + DEAN → Ag(DEAN)<sup>+</sup> + Cu<sub>2</sub>

AgCu<sub>2</sub><sup>+</sup> + DEAN → Ag(DEAN)<sup>+</sup> + Cu<sub>2</sub>

AgCu<sub>2</sub><sup>+</sup> + DAN → Ag(DEAN)<sup>+</sup> + Cu<sub>2</sub>

AgCu<sub>2</sub><sup>+</sup> + AZ → Ag(AZ)<sup>+</sup> + Cu<sub>2</sub>

AgCu<sub>2</sub><sup>+</sup> + AZ → Ag(AZ)<sup>+</sup> + Cu<sub>2</sub>

AgCu<sub>2</sub><sup>+</sup> + DMAN → Ag(DMAN)<sup>+</sup> + AgCu

Ag<sub>2</sub>Cu<sup>+</sup> + DMAN → Ag(DMAN)<sup>+</sup> + AgCu

Cu<sub>2</sub><sup>+</sup> + DMAN → Cu + Cu(DMAN)<sup>+</sup>

Cu<sub>2</sub><sup>+</sup> + m-TOL → Cu + Cu(MAN)<sup>+</sup>

Cu<sub>2</sub><sup>+</sup> + AN → Cu + Cu(AN)<sup>+</sup>
```

<sup>a</sup>DMAN = dimethylaniline; AZ = azulene; *m*-TOL = *m*-toluidine; DEAN = diethylaniline; *m*-DCBZ = *m*-dichlorobenzene; BZ = benzene; FBZ = fluorobenzene; AN = aniline.

TABLE IV: Bond Energies (eV) of Coinage Metal Dimers and Metal-CTA Complexes<sup>c</sup>

species	bond energy	species	bond energy		
Ag <sub>2</sub>	1.65 <sup>2</sup>	Ag(DMAN) <sup>+</sup>	>1.65 <sup>b</sup>		
$Ag_2^+$	$1.65 \pm 0.22^{b}$	$Ag(m-TOL)^+$	>1.65 <sup>b</sup>		
AgCu	1.76 <sup>2</sup>	$Ag(AZ)^+$	>1.65 <sup>b</sup>		
AgCu <sup>+</sup>	$1.91 \pm 0.19^{b}$	Ag(DEAN) <sup>+</sup>	>1.65 <sup>b</sup>		
Cu,	2.03 <sup>2</sup>	$Au(m-DCBZ)^+$	>2.39		
Cu <sub>2</sub> <sup>+</sup>	2.03 🛳 0.15 <sup>b</sup>	Au(BZ) <sup>+</sup>	>2.39 <sup>b</sup>		
Au <sub>2</sub>	2.29 <sup>2</sup>	Au(FBZ)+	>2.39		
Au_2+	$2.39 \pm 0.15^{b}$	Cu(AZ) <sup>∔</sup>	>2.03 <sup>b</sup>		
Ag(DMAN) <sup>+</sup>	$1.67 \pm 0.12^{a}$	Cu(DMAN) <sup>+</sup>	>2.03*		
Ag(m-TOL)+	$1.71 \pm 0.23^{a}$	Cu(m-TOL)+	>2.03 <sup>b</sup>		
Ag(AZ) <sup>+</sup>	$1.61 \pm 0.27^{a}$	Cu(AN)+	>2.03*		

<sup>a</sup>This work by CID. <sup>b</sup>This work by thermochemical analysis. <sup>c</sup>Abbreviations the same as those in Table III.

TABLE V: Rates for Reactions of Charge-Transfer Agents with Various Metal Cluster Ions Resulting in Bond Cleavage. All Rates Are in Units of 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup> and Are Uncorrected for Ion Gauge Sensitivity<sup>a</sup>

$AgCu^+ + DMAN \rightarrow Ag + Cu(DMAN)^+$	4.8 ± 0.4
$AgCu^+ + AZ \rightarrow Ag + Cu(AZ)^+$	4.4 🛳 0.8
$AgCu^+ + m$ -TOL $\rightarrow Ag + Cu(m$ -TOL) <sup>+</sup>	0.8 ± 0.1
$AgCu^+ + DEAN \rightarrow Ag + Cu(DEAN)^+$	$5.5 \pm 0.8$
$Ag_{2}^{+} + DEAN \rightarrow Ag + Ag(DEAN)^{+}$	$0.77 \pm 0.1$
$Ag_{2}^{+} + DMAN \rightarrow Ag + Ag(DEAN)^{+}$	0.55 ± 0.1
$Ag_{2}^{+} + m - TOL \rightarrow Ag + Ag(m - TOL)^{+}$	$0.51 \pm 0.1$
$Ag_{2}^{+} + AZ \rightarrow Ag + Ag(AZ)^{+}$	$0.62 \pm 0.1$
$Au_{3}^{+} + m - DCBZ \rightarrow Au + Au(m - DCBZ)^{+}$	$1.5 \pm 0.1$
$Au_2^+ + BZ \rightarrow Au + Au(BZ)^+$	$0.7 \pm 0.1$
$Au_2^{+} + FBZ \rightarrow Au + Au(FBZ)^{+}$	$1.8 \pm 0.3$
$AgCu_{2}^{+} + DMAN \rightarrow Ag(DMAN)^{+} + Cu_{2}$	$3.8 \pm 0.1$
$AgCu_{2}^{+} + DEAN \rightarrow Ag(DEAN)^{+} + Cu_{2}^{-}$	$2.0 \pm 0.3$
$AgCu_2^+ + m TOL \rightarrow Ag(m TOL)^+ + Cu_2$	$5.1 \pm 1.2$
$AgCu_2^+ + AZ \rightarrow Ag(AZ)^+ + Cu_2$	$1.4 \pm 0.3$
$Ag_2Cu^+ + DMAN \rightarrow Ag(DMAN)^+ + AgCu$	$2.4 \pm 0.2$
$Ag_2Cu^+ + m$ -TOL $\rightarrow Ag(m$ -TOL) + AgCu	2.7 ± 0.4
$Ag_2Cu^+ + AZ \rightarrow Ag(AZ)^+ + AgCu$	$6.5 \pm 0.5$
$Cu_2^+ + DMAN \rightarrow Cu + Cu(DMAN)^+$	$2.1 \pm 0.3$
$Cu_2^+ + m$ -TOL $\rightarrow Cu + Cu(m$ -TOL) <sup>+</sup>	0.8 ± 0.1
$Cu_2^+ + AZ \rightarrow Cu + Cu(AZ)^+$	$1.0 \pm 0.2$
$Cu_{2}^{+} + AN \rightarrow Cu + Cu(AN)^{+}$	$1.4 \pm 0.1$

"Abbreviations the same as those in Table III.

as a check of the range of bond dissociation energies of these complexes derived using eq 3 and observations of cluster reactivity.

<sup>(37)</sup> Hopkins, J. B.; Langridge-Smith, P. R. R.; Morse, M. D.; Smalley, R. E. Unpublished work.

<sup>(38)</sup> Morse, M. D. Advances in Metal and Semiconductor Clusters, Vol.
I. Spectroscopy and Dynamics, in press.
(39) Howard, J. A.; Sutcliffe, R.; Mile, B. Surf. Sci. 1985, 156, 214.

 <sup>(39)</sup> Howard, J. A.; Sutcliffe, R.; Mile, B. Surf. Sci. 1985, 156, 214.
 (40) Walsch, S. P.; Bauschlicher, C. W., Jr.; Langhoff, S. R. J. Chem. Phys. 1986, 85, 5900.

The CID results agree favorably with other results in all cases. Duncan et al.<sup>41</sup> have recently determined a value of slightly less than 2 eV for the upper limit of the silver-benzene bond dissociation energy, in reasonable agreement with the results of this study.

Ion/molecule reaction rates derived similarly to earlier methodology<sup>16</sup> for the various reactions resulting in metal-metal bond cleavage are listed in Table V. All values are less than that predicted for an ion-induced dipole orbiting "Langevin"42 collision. As discussed previously,<sup>16</sup> this observation suggests that charge transfer is not occurring via a long-range electron jump mechanism and thus that adiabatic rather than vertical ionization potentials are indeed being determined.

#### 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. Bracketing may also be

- (42) Langevin, P. M. Ann. Chim. Phys. 1905, 5, 245. Translated in: McDaniel, E. W. Collision Phenomena in Ionized Gases; Wiley: New York, 1964; Appendix II.
- (43) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. J. Phys. Chem. Ref. Data 1988, 17, (Suppl. No. 1).
- (44) Moini, M.; Eyler, J. R. Chem. Phys. Lett. 1987, 137, 311. (45) LaiHing, K.; Cheng, P. Y.; Duncan, M. A. Z. Phys. D: At., Mol.
- Clusters 1989, 13, 161.
  - (46) Cheng, P. Y.; Duncan, M. A. Chem. Phys. Lett. 1988, 341.
- (47) Cheng, P. Y. Dissertation, University of Georgia, 1990.
  (48) Powers, D. E.; Hansen, S. G.; Geusic, M. E.; Michalopoulos, D. L.; Smalley, R. E. J. Chem. Phys. 1983, 78, 2866.

applied to determine other physical properties such as proton and electron affinities of metal clusters. Although direct laser desorption/ionization methods such as those used in this work are limited to the production of relatively small cluster ions, clusters as large as five atoms may be studied effectively. Metal oxide mixtures have been utilized to 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 show good agreement with the few well-known values for these species, indicating a high degree of accuracy for this 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.

Acknowledgment. This research was supported by The Office of Naval Research. We thank Professor W. Weltner for the use of several metal samples and Dr. K. R. Williams for numerous helpful comments.

**Registry No.** Ag<sub>2</sub>, 12187-06-3; Ag<sub>3</sub>, 12595-26-5; Ag<sub>5</sub>, 64475-46-3; Au2, 12187-09-6; Au3, 75024-07-6; Au5, 131359-45-0; Cu2, 12190-70-4; Cu<sub>3</sub>, 66771-03-7; AgCu, 12249-45-5; AgCu<sub>2</sub>, 52373-99-6; Ag<sub>2</sub>Cu, 98002-69-8; ferrocene, 102-54-5; N,N-diethyl-p-toluidine, 613-48-9; N,N-dimethyl-p-toluidine, 99-97-8; N,N-diethylaniline, 91-66-7; N,Ndimethylaniline, 121-69-7; azulene, 275-51-4; m-toluidine, 108-44-1; aniline, 62-53-3; 2-naphthol, 135-19-3; hexamethylbenzene, 87-85-4; p-dichlorobenzene, 106-46-7; 1,2,4-trichlorobenzene, 120-82-1; m-dichlorobenzene, 541-73-1; fluorobenzene, 462-06-6; benzene, 71-43-2; tetrachloroethylene, 127-18-4.

## Structural Determinations for Two Isomeric Forms of N<sub>2</sub>O–HCN

## D. C. Dayton,<sup>†</sup> L. G. Pedersen, and R. E. Miller<sup>\*,‡</sup>

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599 (Received: July 15, 1991)

High-resolution infrared spectroscopy has been used in conjunction with molecular beam techniques to identify two isomers of the  $N_2O$ -HCN binary complex. The more abundant isomer has the two monomer units essentially parallel to one another. The less abundant, and presumably higher energy, isomer is linear with the HCN monomer unit acting as the acid. Isotopic substitution reveals that the hydrogen atom is bonded to the oxygen end of the nitrous oxide subunit. Ab initio calculations have also been carried out for this system, using a number of different basis sets. Comparisons are made between the rotational constants, vibrational frequencies, and relative stabilities of the two isomers.

#### Introduction

Since the dimensionality of intermolecular potential energy surfaces increases rapidly with the complexity of the associated monomer units, one expects that the likelihood of there being more than one local minimum on these surfaces would increase in a similar manner. For systems in which the intermolecular interactions are highly anisotropic, as in hydrogen-bonded complexes, the possibility therefore exists for the formation of more than one stable isomeric form. The large anisotropy is important since high barriers are needed to ensure that the complex can be frozen into the various local minima. A growing number of such systems have recently been studied using a variety of spectroscopic methods.<sup>1-15</sup>

The observation of more than one isomeric form of a complex is important, given that data of this type provide us with information on more than one region of the intermolecular potential. This is particularly significant in molecule-molecule complexes,

- (1) Joyner, C. H.; Dixon, T. A.; Baiocchi, F. A.; Klemperer, W. J. Chem. Phys. 1981, 74, 6550.

  - Lovejoy, C. M.; Nesbitt, D. J. J. Chem. Phys. 1987, 87, 1450.
     Dayton, D. C.; Miller, R. E. Chem. Phys. Lett. 1988, 143, 580.
     Lovejoy, C. M.; Nesbitt, D. J. J. Chem. Phys. 1989, 90, 4671.
- (5) Kukolich, S. G; Bumgarner, R. E.; Pauley, D. J. Chem. Phys. Lett. 1987, 141, 12.
  - (6) Kukolich, S. G.; Pauley, D. J. Chem. Phys. 1989, 131, 403.
     (7) Kukolich, S. G.; Pauley, D. J. J. Chem. Phys. 1989, 90, 3458.
- (8) Leopold, K. R.; Fraser, G. T.; Klemperer, W. J. Chem. Phys. 1984, *80*, 1039
- (9) Klots, T. D.; Ruoff, R. S.; Gutowsky, H. S. J. Chem. Phys. 1989, 90, 4217
- (10) Dayton, D. C.; Pedersen, L. G.; Miller, R. E. J. Chem. Phys. 1990, 93. 4560.
- (11) Haynam, C. A.; Brumbaugh, D. V.; Levy, D. H. J. Chem. Phys. 1983, 79, 1581; Levy, D. H. J. Chem. Soc., Faraday Trans. 1986, 82, 1107.
   (12) Aldrich, P. D.; Kukolich, S. G.; Campbell, E. J. J. Chem. Phys. 1983, 78, 3521.
- 0022-3654/92/2096-1087\$03.00/0 © 1992 American Chemical Society

<sup>(41)</sup> Duncan, M. J. Phys. Chem. 1990, 94, 4769.

<sup>&</sup>lt;sup>†</sup>Present address: U.S. Army Ballistic Research Laboratory, SLCBR-IB-I, Aberdeen Proving Ground, MD 21005-5066. \* To whom correspondence should be addressed.

<sup>&</sup>lt;sup>‡</sup>Alfred P. Sloan Fellow.