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Photodissociation of silver–coronene cluster cations

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Abstract

Gas phase complexes of coronene and silver are produced in a molecular beam and studied with time-of-flight mass spectrometry and laser photodissociation. The cation complexes are produced in a pulsed nozzle laser vaporization cluster source using a silver rod coated with a sublimed film of coronene. Cluster masses of the form Ag_x–$(cor)_y^+$ are observed for $x = 0, 1, 2$ and $y = 1$–3. Mass-selected photodissociation experiments probe the structure and bonding in these new cluster species. These studies demonstrate that silver binds weakly to coronene and that cation clusters of pure coronene have substantial stability. (Int J Mass Spectrom 185/186/187 (1999) 617–624) © 1999 Elsevier Science B.V.

Keywords: Clusters; Photodissociation; Time-of-flight mass spectrometry

1. Introduction

Organometallic π complexes have stimulated interest for many years [1–3]. Recently, molecular beam techniques have made it possible to synthesize unusual new complexes in the gas phase and to investigate their spectroscopy and photochemistry. Metal benzene complexes or those with other small aromatic systems have been known and studied for many years [2–8]. In new developments, Kaya and co-workers have produced remarkable multidecker complexes with benzene [9]. Bowers and co-workers have investigated these species with ion chromatography methods and have confirmed the multidecker sandwich structures proposed by Kaya [10]. Mass spectrometry experiments have also produced metal complexes with larger aromatic systems including polyaromatic hydrocarbons (PAHs) [11] and fullerenes [12–17]. With laser or oven sources designed for higher metal densities, Martin and co-workers have produced multiple metal atom films and even multilayer films on the surface of C_{60} [15]. Our research group has investigated the photodissociation dynamics of such species [16]. Kaya and co-workers have also generated metal–C_{60}–metal–C_{60} networks [17]. These various species have promise for the synthesis of cluster assembled materials. However, the characterization of their structure and bonding remains a significant challenge.

We have recently extended these concepts to produce metal complexes in the gas phase with a variety of polyaromatic hydrocarbon molecules (PAHs; coronene, pyrene, phenanthrene, etc.) [18]. In the present article, we describe complexes having one or more silver atoms bound to coronene ($C_{24}H_{12}$). In an earlier article, we described complexes of coronene with iron

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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atoms [18]. Because of the extended aromatic system of coronene, multiple binding sites are present offering varied possibilities for organometallic bonding. Photodissociation studies investigate the bonding in these species and provide a comparison with the behavior of related iron–coronene complexes.

Polyaromatic hydrocarbons are present in a variety of environments such as sooty flames and automobile exhausts. They are stable enough to survive in high temperature environments. The optical properties of PAHs have been investigated in solution, in high temperature gases and in cryogenic matrices [19–28]. In astrophysical spectroscopy, neutral and/or cation PAH species have been proposed as carriers for the unidentified infrared lines (UIRs) or the optical diffuse interstellar bands (DIBs) [21,22,27,28]. However, recent studies have shown that the measured spectra of isolated PAH molecules or their ions do not match precisely with the astrophysical spectra. Complexes with PAH species, including those containing metals, have been proposed as alternative carriers for the unidentified spectra [20]. However, a general source of gas phase PAH molecules and/or complexes in neutral or ionized form at the required low temperatures of the interstellar medium (50–100 K) has not been available previously to test these proposals.

Coronene complexes with metal ions have been studied previously by Dunbar and co-workers [11]. Metal ions were produced by laser vaporization and interacted with a low pressure of coronene vapor sublimed from an oven in a Fourier transform mass spectrometer (FTMS). Radiative association kinetics were measured for a variety of transition metal and main group metal cations. Addition of one or two coronene molecules to a single metal ion was observed. In the present study, metal–coronene complexes are produced by laser vaporization of a composite sample in a pulsed nozzle cluster source. Species produced from this source are supersonically cooled and the prospect exists for spectroscopic studies. Photodissociation in a reflectron time-of-flight mass spectrometer makes it possible to investigate the dissociation pathways and qualitative bonding strengths in these complexes.

2. Experimental

Silver–coronene complexes are produced in a laser vaporization cluster source with specially prepared samples. A pure silver rod (1/4 in. in diameter) is coated with a sublimed film of coronene using a small vacuum chamber dedicated for sample preparation. A sublimation oven is constructed from a 1/4-in.-diameter ceramic tube wrapped with a nichrome wire heater and controlled with a variac. The oven is loaded with coronene powder (Aldrich) and heated until visible sublimation occurs on the vacuum chamber windows. The sample rod is mounted on a rotating stage about 2 in. from the oven. The resulting film thickness is approximately 0.1 mm.

The film coated sample rod is transferred to a molecular beam machine and mounted in a laser vaporization cluster source. This source is of standard design, but uses a modified Newport nozzle [16]. Vaporization is accomplished with the third harmonic of a Nd:YAG laser at 355 nm. We use laser powers lower than those employed for pure metal vaporization, but higher than those used for matrix-assisted laser desorption ionization (MALDI) experiments (about 10 mJ/pulse). The conditions are similar to those recently described for Ag_x–C_{60} complex formation where signals are sensitive to both film thickness and the vaporization laser power [16]. Under optimized conditions the vaporization laser desorbs coronene and penetrates through to ablate the underlying metal, thus producing both species in the gas phase which recombine in the growth channel region of the source. Cation clusters are produced directly in the source plasma without any postionization. The species produced pass through a skimmer and are extracted from the molecular beam into the mass spectrometer with pulsed acceleration voltages. The beam apparatus for these experiments was described previously [5].

Specific cluster ions are mass selected with a specially designed reflectron time-of-flight mass spectrometer for photodissociation studies [5]. A pulsed deflection plate assembly located at the end of the first flight tube transmits only the ions of interest, which are then excited with a pulsed Nd:YAG laser (532 or

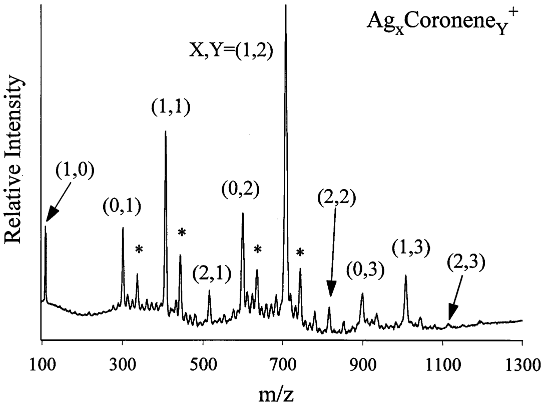

Fig. 1. The mass spectrum of silver–coronene cation clusters produced by vaporizing a film-coated sample rod. The masses indicate the formation of silver–coronene cation clusters and coronene cation clusters.

355 nm) in the turning region of the reflectron field. The time of flight through the second arm of the reflectron determines the masses of photofragments.

3. Results and discussion

The first observation about silver–coronene complexes is that they are produced under conditions noticeably different from the previously studied iron–coronene clusters. Iron–coronene complexes grow most efficiently with a wide (4 mm) extension channel attached to the laser vaporization cluster source using conditions similar to those used to produce pure metal clusters. Silver–coronene complexes do not grow efficiently under these conditions but instead require a shorter growth channel (3 mm) with a narrower diameter (2 mm). This type of source produces a colder expansion and is like that used to produce weakly bound metal ion–rare gas complexes [29]. This observation suggests that silver binds more weakly to coronene than iron does. Dunbar also concluded that silver–coronene interactions are weak compared to the interactions of coronene with other transition metals [11].

The mass spectrum of cation silver–coronene complexes produced with an optimized source is shown in Fig. 1. The labeling system indicates the stoichiometry of Ag_x–$(cor)_y^+$ complexes as (x, y). In the lower mass region, the silver atomic ion is observed with weak intensity. At higher mass, cations representing the pure coronene cation, coronene cluster cations and various silver–coronene complexes are observed. The masses labeled with asterisks correspond to adducts of potassium with these complexes from an impurity in the sample, most likely coming from the oven used for film preparation. Ag–$(cor)^+$ is especially prominent, as are Ag–$(cor)_2^+$ and Ag–$(cor)_3^+$. It is clear from this mass spectrum that silver and coronene form a variety of mixed complexes. There is little evidence for fragmentation of coronene in the laser plasma or by reactions with silver, which could conceivably produce smaller hydrocarbon or metal–hydrocarbon species. The clean production of metal–coronene adducts has also been observed from this same production method with metals such as iron, chromium, nickel, bismuth, and calcium. However, when a niobium rod coated with coronene is vaporized, many metal carbide fragments are observed in the mass spectrum [30]. Niobium is well known to form strongly bound metal carbides, especially including the "met–cars" clusters, while these other metals have only a weak tendency in this regard [31].

In the high mass region of this spectrum, it can be seen that there are no clusters produced containing more than two to three silver atoms. This is in marked contrast to mass spectra we have measured for coronene in complexes with other transition metals (iron, chromium, vanadium, etc.), where as many as four to six metals are seen in combination with one coronene in peaks with strong intensity. Apparently, silver atoms and/or clusters do not bind as strongly as these other transition metals to coronene.

We use mass-selected photodissociation measurements to investigate more fully the properties of these silver complexes. Fig. 2 shows the photodissociation of Ag–$(cor)^+$ at 355 nm. This data is accumulated as a difference spectrum with and without the photodissociation laser. The negative peak represents the depletion of the mass selected parent ion, while the positive peaks represent the photofragments. The photodissociation signal measured here is much weaker than that of similar silver–benzene complexes

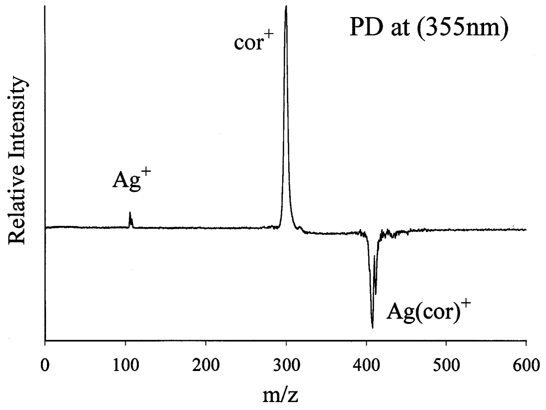

Fig. 2. The photodissociation mass spectrum of [Ag–coronene]$^+$ at 355 nm. The most intense fragment is the coronene cation, but a small amount of Ag$^+$ is also observed.

which we have studied previously [5]. Only higher laser powers are effective in producing photodissociation, consistent with a multiphoton process. The fragmentation products observed include the bare silver cation and the more prominent coronene cation, with no evidence for metal–carbide or metal–hydrocarbon fragments. This fragmentation indicates again that no extensive rearrangement has taken place in the coronene system. Silver has an ionization potential of 7.58 eV, while that of coronene is 7.29 eV. Because of the close proximity of these numbers, it is not surprising that both Ag$^+$ and the coronene cation can be observed as charged fragments. However, the lower ionization potential (IP) of coronene leads to more efficient production of this species as the charge carrier. The inefficiency of fragmentation in this complex is expected if the dissociation is unimolecular with randomization of energy prior to bond breaking. For such a large molecule, high excess energy is required to cause fragmentation on the timescale (about 2–3 μs) required for observation in the time-of-flight instrument. In this scenario, dissociation is expected to occur by the lowest energetic pathway in the ground electronic state. We cannot prove from our data that this is the case here. However, even though the dissociation process is most likely multiphoton in nature, the expected lowest energy process (coronene cation with neutral silver) is indeed observed to be dominant.

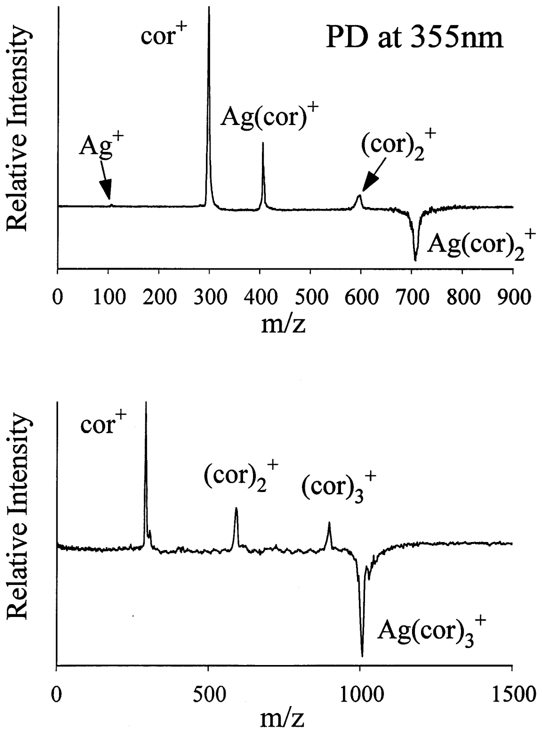

Fig. 3. The photodissociation mass spectrum of [Ag–cor$_2$]$^+$ and [Ag–cor$_3$]$^+$ at 355 nm.

The prominence of Ag–(cor)$_2^+$ in the mass spectrum naturally raises the question of sandwich structures. We are therefore interested to investigate the stability of this complex and to see if it is produced as a stable fragment from larger complexes. Fig. 3 shows the photodissociation mass spectra of Ag–(cor)$_2^+$ and Ag–(cor)$_3^+$ cations at 355 nm. As above, these data are necessarily accumulated at high laser powers to overcome the low cross section for photodissociation. The upper trace shows the dissociation of Ag–(cor)$_2^+$. We find the prominent production of the coronene cation, but there are also other smaller fragment peaks. Because of the high laser power, these various fragment ions may be produced directly from the parent ion in parallel fragmentation channels, or they may represent ions produced by a sequence of multiple fragmentation steps. It is impossible for us to distinguish these processes, although we work at the lowest laser powers possible to minimize sequential process. Thus, coronene cation could be produced from Ag–

$(cor)_2^+$ by loss of neutral Ag–cor, or it could be produced in a sequential process by additional fragmentation of the Ag–$(cor)^+$ fragment ion. It would be surprising if Ag–cor were produced efficiently as both an ionized and neutral fragment, and so the latter process is more likely.

The surprising fragment observed is a small amount of the coronene dimer cation, which can only be formed by elimination of the neutral silver atom. As described previously, coronene has a lower ionization potential than silver, and clusters usually have lower IPs than corresponding monomers, so the elimination of neutral silver is not too surprising. However, it is surprising to see this dimer complex at all. We have studied multicoronene complexes with a variety of metals, and have not observed $(cor)_x^+$ fragments for any other system. The elimination of silver could conceivably come from either a sandwich or nonsandwich structure, and there could be isomerization during dissociation, so this fragment does not provide much insight into the complex structure. We presume that coronene–coronene$^+$ bonding is electrostatic in nature, although we cannot rule out the possibility of covalent dimer formation. Polymerization of PAH systems smaller than coronene (e.g. anthracene) is known in condensed phase chemistry [19,20]. If dimerization has occurred here, silver would be unique among the metals we have studied in catalyzing this process. However, a more likely explanation for the production of $(cor)_2^+$ is that it is just an electrostatic complex bound by the resonant charge-induced dipole interaction between the two rings. If this is the case, then the binding of a silver atom to coronene is not only weak compared to that of other metals we have studied (iron, chromium, vanadium, calcium, niobium), it is also weak compared to coronene–coronene$^+$ bonding. Weak interactions relative to other transition metals were also found in our previous studies of the binding between silver and C_{60} [16] and in the binding of silver to benzene [4–8]. Dunbar has also found that silver binds more weakly to coronene than other transition metals. Using his "standard hydrocarbon model" of association reaction rates, he has suggested a bond energy for Ag–$(cor)^+$ of about 32 kcal/mol [11]. With this number then, we can suggest that the coronene dimer cation bond energy is $\geq$32 kcal/mol. This is much larger than the benzene dimer cation bond energy of 15.2 kcal/mol [32].

The lower trace of Fig. 3 shows the photodissociation of Ag–$(cor)_3^+$ complexes. Dramatically, there are no metal-containing fragments observed at all. The fragment ions detected include coronene trimer, dimer and monomer units, which again could be produced in parallel or as a sequence. This data again suggests that neutral silver atom has been eliminated from these complexes and that its binding is weak compared to the coronene–coronene interactions. In data not shown, we observe a similar fragmentation process for Ag–$(cor)_4^+$, where the fragments are $(cor)_4^+$, $(cor)_3^+$, $(cor)_2^+$ and cor^+, with no retention of metal. These results are dramatically different from our results on Fe–$(cor)_x^+$ clusters, where the magic numbered ion Fe–$(cor)_2^+$ (presumed to represent a sandwich complex) was observed as the only fragment from all larger species.

In the fragmentation systems here where $(cor)_x^+$ species are produced, we are unable to distinguish between covalently linked polymerized coronene and simple electrostatically bound complexes. However, polymerization at multiple sites in such a large cluster on the short timescale of fragmentation seems extremely unlikely, and we therefore assume that these $(cor)_x^+$ species represent electrostatic complexes. Additional fragmentation studies of the $(cor)_x^+$ complexes produced this way would of course be interesting to address the possibility of polymerization versus simple electrostatic complex formation, but our instrumentation does not allow such experiments. However, we have also observed efficient formation of $(cor)_x^+$ complexes from ablation of thick coronene films with no metal present. These species fragment by loss of intact coronene units, providing no evidence for polymerization. The ease of formation of $(cor)_x^+$ complexes is not surprising considering the large surface area and presumably high polarizability of coronene. We have also observed efficient formation of neutral coronene clusters detected with multiphoton ionization (ArF; 193 nm). Coronene clusters are therefore easily produced in neutral or charged

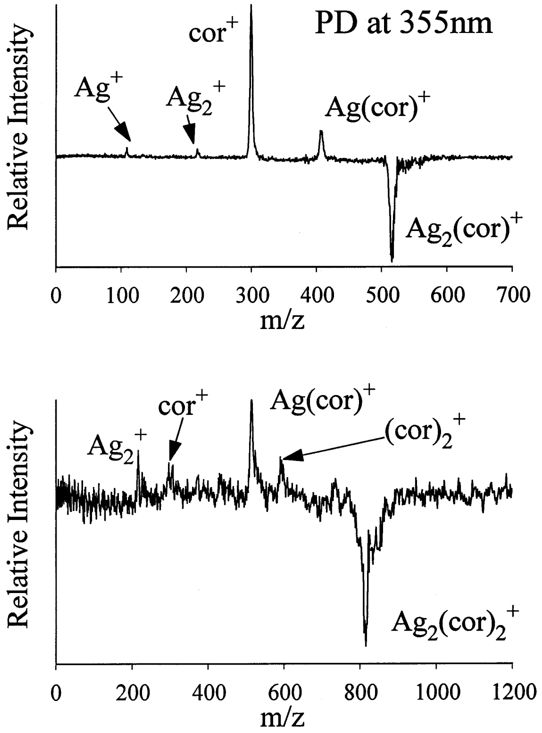

Fig. 4. The photodissociation of [Ag$_2$–cor]$^+$ and [Ag$_2$–cor$_2$]$^+$ at 355 nm.

varieties. The structures of such complexes might be parallel plates like graphite, or they might be herringbone staggered arrangements like solid benzene and benzene clusters. It would be interesting to explore these possibilities with a method such as ion chromatography (also known as ion mobility) [33,34].

More interesting structural possibilities arise for multisilver/multicoronene complexes. Fig. 4 shows the photodissociation of Ag$_2$–(cor)$^+$ and Ag$_2$–(cor)$_2^+$ complexes. The signal-to-noise ration is much better in the upper trace, which shows that Ag$_2$–(cor)$^+$ dissociates to produce primarily the coronene cation. The neutral fragment(s) accompanying this cation could either be two silver atoms or the diatomic Ag$_2$ molecule. Elimination of molecular species is the lower energy process. Other weaker fragments include Ag$^+$, Ag$_2^+$, and Ag–cor$^+$. Of these, the Ag$_2^+$ species is perhaps most interesting. The IP of Ag$_2$ is 7.66 eV [35], which is close to but greater than those of Ag and coronene. It is conceivable then that some Ag$_2$ is eliminated directly which is charged. Another mechanism for production of Ag$_2^+$ is elimination of Ag$_2$ neutral, which then becomes multiphoton ionized in the intense ultraviolet laser used for photofragmentation. When Ag$_2$–(cor)$^+$ is photodissociated at 532 nm, this fragmentation pattern changes somewhat. Only two channels are observed, with a strong signal for Ag–(cor)$^+$ and a weaker one for (cor)$^+$. The fragmentation at 532 nm is also multiphoton in nature, but the photon energy is lower and the average energy input is less. The main fragmentation here is loss of silver atom and there is no detection of Ag$_2^+$. If Ag$_2$ is formed at all here, it must be as a neutral rather than as an ion. This wavelength dependence on the signal calls attention to the potential dangers of interpreting these fragmentation patterns.

The lower trace of Fig. 4 has weak signal levels, but the fragmentation products show that coronene monomer and dimer cations, Ag–(cor)$^+$ and Ag$_2^+$ are produced. Again, some silver–silver bonds are preserved and coronene dimer is observed. The simultaneous observation of ions such as Ag$_2^+$, Ag–(cor)$^+$ and (cor)$_2^+$, which must result from parallel fragmentation channels, suggests that these species have similar bond energies. Of these, there is known thermochemistry for Ag$_2^+$. Using the measured dissociation energy for Ag$_2$ (38.3 kcal/mol [36]) in an energetic cycle with the IPs of Ag atom and Ag$_2$, the dissociation energy of Ag$_2^+$ turns out to be about 36 kcal/mol. This bond energy is close to the estimate for the Ag–(cor)$^+$ bond.

In very noisy data not shown, we have been able to photodissociate Ag$_3$–(cor)$^+$ at 532 nm. The fragments seen are coronene cation and Ag–cor$^+$. The coronene cation could be accompanied by three neutral silver atoms, by one atom and Ag$_2$, or by Ag$_3$. In this case, however, we are able to gain some insight from the known ionization energies of Ag$_3$. As mentioned above, Ag and Ag$_2$ have IPs near 7.6 eV, which are not too different from the IP of coronene. Ag$_3$ however, has an IP near 6.0 eV [37], which is significantly less than that of coronene. If Ag$_3$ is eliminated, it should carry the charge in the form of Ag$_3^+$. Ag$_3^+$ was observed as the primary photoproduct in previous studies of $[Ag_3–C_{60}]^+$ [16]. However, this ion is not observed here. The fragments from Ag_3–$(cor)^+$ must then be either neutral atomic or diatomic silver.

It is clear from these various fragmentation processes that silver–coronene interactions in these cation complexes are weak compared to those with other transition metals, that silver–coronene interactions are close in energy to silver–silver interactions and that coronene–coronene interaction are stronger. These observations are understandable in light of the electronic structure of silver and the ionization energetics of small silver molecules. Silver has a closed *d* shell, and is therefore less effective in accepting ligand π electron density than metals such as iron or chromium. Its metal–ligand bonding is therefore weaker. This effect also explains the weaker binding in Ag–$(benzene)^+$ (37 kcal/mol) than in Fe–$(benzene)^+$ (49 kcal/mol) [5–7]. Without the possibility for covalent bonding, only electrostatic interactions are available to bind the silver complexes. In the Ag–$(cor)^+$ complex, the ionization potentials for silver (7.58 eV) and coronene (7.29 eV) suggest that the charge in the complex is localized more on coronene than it is on silver. The electrostatic interaction of interest is then that between a delocalized charge on the coronene π system polarizing a neutral silver atom, which should be a relatively weak interaction. This is in contrast to the binding in a complex such as Ag–$(benzene)^+$, where the benzene IP is much greater than that in silver, and the electrostatic bonding is between a charged metal atom and a large polarizable neutral molecule. We would therefore expect the silver–$coronene^+$ binding to be weaker than the silver–$benzene^+$ binding (about 37 kcal/mol [5–7]). This same reasoning explains how a complex like Ag–$(cor)_2^+$ or Ag–$(cor)_3^+$ can eliminate silver and retain the coronene cluster. When the charge is localized more on coronene, charge induced polarization of the other coronene molecule(s) is more efficient than that for the silver atom. The same argument applies for complexes of the form Ag_2–$(cor)_x^+$. Whether the silver is present as two atoms or as Ag_2, the IPs are about the same, and the charge would again be on the molecule, resulting in weak electrostatic interactions. For Ag_3–$(cor)_x^+$ complexes (only studied here for $x = 1$), the strong binding in silver trimer cation and the low IP of Ag_3 (6 eV) suggest that at least some of the clusters may be considered as Ag_3^+–coronene. In this case the electrostatic interactions would be relatively strong. If larger Ag_3–$(cor)_x^+$ complexes could be produced for $x \geq 2$, production of $(cor)_x^+$ fragments may not be so efficient.

4. Conclusions

Laser vaporization of film-coated metal samples makes it possible to produce jet-cooled silver–coronene cation complexes and coronene cluster cation complexes in the cold supersonic molecular beam environment. Time-of-flight mass spectrometry reveals the species formed, which include complexes with up to three silver atoms and up to four coronene molecules. Mass selected photodissociation in a reflectron time-of-flight instrument allows investigation of the relative stability of these complexes. Photodissociation produces no magic number metal–coronene species, in contrast to previous studies on iron–coronene species. Surprising photodissociation channels include the elimination of silver atom or silver dimer from mixed clusters with the resulting formation of pure coronene cluster cations. The results of these various studies indicate that silver–coronene binding interactions are much weaker than other transition metal–coronene interactions, consistent with a bond energy of about 32 kcal/mol suggested previously by Dunbar. Coronene cation clusters have significant stability in their own right, with the bond energy for $(cor)_2^+$ indicated to be greater than that for Ag–$(cor)^+$. The structures of these species are the subject of speculation now, because there is no direct information from our data. These systems are ideal candidates for ion chromatography/ion mobility studies like those performed by Bowers and coworkers or Jarrold and co-workers on other large gas phase clusters to investigate their structures. Future studies may also investigate the wavelength dependent spectroscopy of these complexes.

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