

## COMMUNICATIONS

**The ultraviolet photofragmentation of doubly charged transition metal complexes in the gas phase: Initial results for  $[\text{Cu}(\text{pyridine})_n]^{2+}$  and  $[\text{Ag}(\text{pyridine})_n]^{2+}$  ions**

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Results are presented of a study of the UV photofragmentation patterns of the doubly charged complexes  $[\text{Cu}(\text{pyridine})_n]^{2+}$  and  $[\text{Ag}(\text{pyridine})_n]^{2+}$  for  $n=4-7$ . The two systems behave very differently, with Ag(II) being dominated by the presence of charge transfer products at small values of  $n$ . This ease of reduction of Ag(II) can be equated to behavior seen in the condensed phase. At all values of  $n$  both types of complex display a remarkable tendency to fragment to the most stable configuration, which can correspond to either a singly or doubly charged ion. © 2000 American Institute of Physics. [S0021-9606(00)01418-5]

A number of recent experiments have sought to extend the realm of gas phase transition metal ion chemistry to examples where the ion occupies an oxidation state that is more characteristic of the metal concerned, i.e., Cu(II), Fe(II), Mg(II), etc., when found in solution.<sup>1-11</sup> Despite the technical difficulties presented by this requirement, significant advances have been made, and a broad range of metal-ligand complexes have been prepared. Experiments of this nature offer opportunities for studying, in the gas phase, many of the fundamental spectroscopic and chemical processes traditionally associated with transition metal ions in the condensed phase.<sup>12</sup>

Arguably one of the most interesting prospects for these new experiments is a detailed understanding of the electronic properties of multiply charged transition metal complexes, and how, for example  $d-d$  and metal/ligand electronic transitions evolve as a function of the nature and number of coordinating molecules. To date, only Posey and co-workers<sup>10,11</sup> have demonstrated the feasibility of such experiments through the use of dissociation as a signature of photon absorption on the part of the complex. Their work has concentrated primarily on exploring the influence of solvent molecules on metal-ligand charge transfer processes, and has not specifically addressed the nature of the metal-ligand interaction. One of the key features of gas phase metal-ligand complexes of the form  $[\text{M.L}_n]^{2+}$  is the presence of a critical value for  $n$  ( $n_{\text{crit}}$  typically  $\leq 3$ ), below which ions are unstable with respect to dissociative charge transfer.<sup>9</sup> The process of charge transfer can be driven by collisional activation and is a characteristic of all  $[\text{M.L}_n]^{2+}$  complexes when  $n$  is  $\leq 8$ , and fragmentation is accompanied by a large release of kinetic energy due to Coulomb explosion. Under these circumstances, the primary role of collisional activation is thought to be that of surmounting the barrier which exists between the doubly and singly charged forms of the

solvated metal, and this is done most effectively by reducing  $n$  to below  $n_{\text{crit}}$ .<sup>9</sup>

With regard to photoexcitation, a more subtle response might be anticipated.<sup>13</sup> For a given  $[\text{M.L}_n]^{2+}$  complex in solution, electronic excitation within the metal ion center could result in metal-to-ligand charge transfer (MLCT), whereas a similar transition in a ligand could lead to ligand-to-metal charge transfer (LMCT).<sup>13</sup> Either process will depend on the degree of overlap between the orbitals involved, and may also depend indirectly upon the rates of radiative and nonradiative relaxation. Examining such transitions in the gas phase without the influence of a solvent on the ligands, should provide for a more accurate evaluation of the metal-ligand interaction. Presented here are the results of a study where, for the first time, it has been possible to photoexcite size-selected  $[\text{M.L}_n]^{2+}$  ions, and examine the competition between LMCT processes and neutral ligand loss induced by rapid nonradiative decay. Two systems have been studied;  $[\text{Cu}(\text{pyridine})_n]^{2+}$  and  $[\text{Ag}(\text{pyridine})_n]^{2+}$ , and tunable UV radiation at  $\sim 280$  nm has been used to promote a  $\pi \rightarrow \pi^*$  transition in the pyridine molecule. The two metal-ligand systems behave differently in their response to ligand excitation; they both, however, display a marked correlation between fragmentation pattern and the underlying presence of a stable  $[\text{M.L}_n]^{2+}$  configuration. Photo-induced dissociative charge transfer in singly charged silver complexes has been observed previously by Duncan and co-workers,<sup>14</sup> and by Afzaal and Freiser,<sup>15</sup> and of direct relevance to the work presented here, are the recent experiments of Yang and Yeh on photo-induced charge transfer in the Ag-pyridine complex.<sup>16</sup>

The experiments have been performed on an apparatus which combines high resolution mass spectrometry with a facility for generating metal-containing clusters. A detailed description of the apparatus and method of preparation has been given previously;<sup>9</sup> therefore, only a very brief summary

is presented here. Neutral clusters of pyridine are formed via the adiabatic expansion of a mixture with argon through a pulsed supersonic nozzle. After passing through a 1 mm diam skimmer the cluster beam enters a drift region where a Knudsen cell is located that contains the metal of interest. The cell is heated to either 1400 °C (Cu) or 1150 °C (Ag) to provide a vapor pressure of approximately  $10^{-2}$  mbar, which is sufficient for the neutral clusters to “pick-up,” on average a single metal atom.

Pure and heterogeneous clusters emerge from the “pick-up” region and pass into the ion source of a high resolution double focusing mass spectrometer (VG ZAB-E) where they are ionized by 100 eV electron impact. The resulting mass spectra are found to contain large numbers of singly charged ions, together with sequences of the general form  $[M.L_n]^{2+}$ , which are stable because the multiply charged metal ion is prepared already encapsulated in a solvent environment. The presence of a double charge is confirmed in two ways. First, mass analyzed ion kinetic energy (MIKE) (Ref. 17) spectra show the presence of unimolecular reaction products (predominantly the loss of  $L$ ) at kinetic energy intervals half those predicted for a singly charged ion. Second, each metal has at least one isotope with an odd mass, and ions containing these appear in the mass spectra at one-half amu intervals.

The use of a high-resolution double focusing mass spectrometer has proved invaluable in this series of experiments.<sup>9</sup> The instrument has the capability to separate out individual multiply charged ions containing up to 30 solvent molecules. In addition, the geometry of a magnetic sector followed by an electrostatic analyzer means that size-selected ions can be photoexcited using a laser, and any subsequent fragmentation detected via a change in kinetic energy. The MIKE technique was used extensively in earlier experiments to investigate the collision-induced reactions of doubly charged metal-containing ions, and in the results presented here the same approach has been used to monitor the effects of laser excitation. Laser radiation with a tuning range of 275–285 nm was generated by frequency-doubling the output from a dye laser (SIRAH-PrecisionScan) pumped with a Nd:YAG laser (Spectron SL805) operating at 532 nm. To maximize the possibility of detecting a response from a weak ion signal ( $\sim 10^{-11}$  A), the laser beam was passed through the mass spectrometer orientated co-axially with the ion beam. With the ion source potential fixed at 5 kV, singly charged decomposition products originating from charge transfer within a mass-selected doubly charged parent ion, were identified by sweeping the voltage on the electrostatic analyzer between  $2E_0$  and zero, where  $E_0$  is the value used to transmit the main ion beam.<sup>17</sup> Signals were detected from a scintillation (Daly) ion detection system operated in conjunction with a fast photomultiplier tube. Data collection on individual photofragments employed a multichannel scalar (Stanford Research SR400) which was triggered, together with the YAG laser, via a delay generator (Stanford Research DG 535). The use of a scalar made it possible to accommodate the large variations in the arrival times of fragments that may result from either Coulomb explosion and/or photoexcitation at dif-

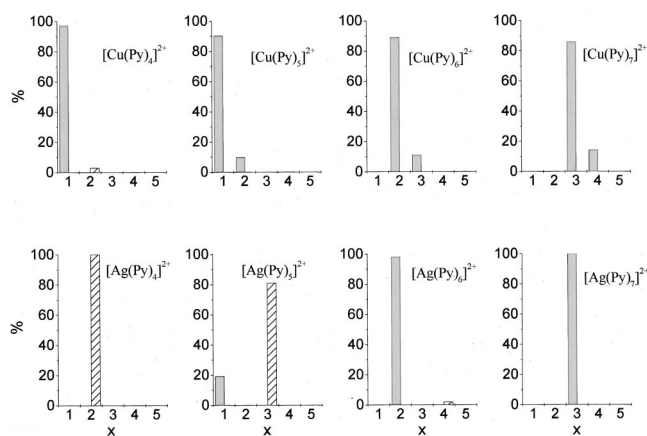


FIG. 1. Relative intensities of photofragments following the excitation of selected  $[\text{Cu}(\text{pyridine})_n]^{2+}$  and  $[\text{Ag}(\text{pyridine})_n]^{2+}$  complexes at 280 nm. Each plot shows the number of molecules lost,  $x$ , either all in the form of neutral molecules (solid lines) or accompanied by one charge transfer product (shaded lines).

ferent positions over the 1.5 m that the ion and laser beams overlap.

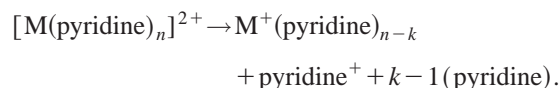
Figure 1 summarizes the fragmentation patterns recorded following the photoexcitation at 280 nm of size-selected  $[\text{M}(\text{pyridine})_n]^{2+}$  complexes for  $n$  in the range 4–7. Two quite separate processes are observed.

- (1) Photo-induced unimolecular decay,



and

- (2) Photo-induced charge transfer (LMCT),



No significant differences in behavior were observed at other wavelengths within the available tuning range of 275–285 nm. Radiation at UV wavelengths is known to promote pyridine to either the  $S_1(n\pi^*)$  state ( $\sim 287$  nm in the gas phase) or the  $S_2(\pi\pi^*)$  state ( $\sim 260$  nm in the gas phase). Both electronic transitions have been the subject of recent work by Chachisvilis and Zewail,<sup>18</sup> where it has been shown that excited pyridine molecules can undergo very rapid non-radiative deactivation ( $\leq 20$  ps) either via intersystem crossing or through the formation of a valence isomer of pyridine. In their study of the singly charged  $\text{Ag}^+$ -pyridine complex at  $\sim 280$  nm, Yang and Yeh suggested they were exciting the  $S_1(n\pi^*)$  state.<sup>16</sup> However, the comparatively small difference between the ionization energies of silver and pyridine means that this system also has a low energy charge transfer band, which complexes may be excited to or could decay from following an intersystem crossing. No similar charge transfer bands exist for complexes with either Cu(II) or Ag(II) because of the large differences in ionization energy for step  $\text{Cu(I)} \rightarrow \text{Cu(II)}$  (20.29 eV) or  $\text{Ag(I)} \rightarrow \text{Ag(II)}$  (21.5 eV) compared with pyridine (9.26 eV).

Two observations lead us to believe that for pyridine molecules in the first solvation shell surrounding either

Cu(II) or Ag(II) we are probably exciting the  $S_2(\pi\pi^*)$  state at  $\sim 280$  nm (see below): (i) Chachisvilis and Zewail recorded absorption spectra for the pyridinium ion and concluded that the  $n\pi^*$  states were missing because the lone-pair electrons on the nitrogen atom are participating in bond formation with the proton. Similarly,  $\text{Cu}^{2+}$  and  $\text{Ag}^{2+}$  can be expected to polarize electron density away from the nitrogen atom on pyridine; however, this effect may not extend to molecules in the second solvation shell; (ii) Schläfer and König concluded from their study that the  $\pi \rightarrow \pi^*$  transition in Cu(II)/pyridine complexes is shifted to longer wavelengths when compared with the free ligand.<sup>19,20</sup> Related work on  $[\text{M}(\text{acetone})_n]^{2+}$  complexes shows that  $n \rightarrow \pi^*$  transitions are strongly influenced by the close proximity of a doubly charged metal ion.<sup>21</sup>

Each  $[\text{M}(\text{pyridine})_n]^{2+}$  ion responds differently to excitation of the ligand. Given the presence of a fast radiationless transition,<sup>18</sup> the most obvious outcome would be for the complex to undergo unimolecular decay, using the excess energy provided by the photon to overcome the binding energy of the ligand. Since both metals have stable  $[\text{M}(\text{pyridine})_3]^{2+}$  ions,<sup>9,22</sup> the loss of one molecule from each tetramer should not, in itself, promote dissociative charge transfer. In this respect, the data presented for the  $[\text{Cu}(\text{pyridine})_n]^{2+}$  ions match expectations; the photoexcited tetramer loses one neutral molecule with only slight evidence of charge transfer accompanying the loss of two pyridines. As the complexes increase in size, the fragmentation pattern undergoes a series of very abrupt transitions in a way which always leaves  $[\text{Cu}(\text{pyridine})_4]^{2+}$  as the dominant (>80%) photofragment. Thus, the larger complexes always decay in a very precise fashion to what is perceived to be the most stable structure.<sup>22</sup>

The data recorded for  $[\text{Ag}(\text{pyridine})_n]^{2+}$  ions contrasts with that given for Cu(II), in that both  $[\text{Ag}(\text{pyridine})_4]^{2+}$  and  $[\text{Ag}(\text{pyridine})_5]^{2+}$  show strong evidence of charge transfer. The fact that the Ag(II) tetramer is recognized as being stable both in the gas phase experiments and in the condensed phase,<sup>9,23,24</sup> means that the observation of charge transfer in  $[\text{Ag}(\text{pyridine})_5]^{2+}$  is unexpected if the mechanism is purely dissociative. The most obvious alternative, is to propose that one or more of the  $4d$  orbitals on Ag(II) lie close in energy to the pyridine  $\pi^*$  orbital which receives the electron in the initial excitation step. Under these circumstances, the extremely short time scale for direct electron transfer would be very effective at reducing Ag(II) to Ag(I), even when compared with the rapid radiationless decay rate exhibited by pyridine in the  $\pi^*$  state.<sup>18</sup> An increased level of interaction between the  $\pi$  orbitals on pyridine and a  $4d$  as opposed to a  $3d$  orbital, would certainly be consistent with both the spectroscopic observations and calculations of Schläfer and König.<sup>19,20</sup> Likewise, the ease of reduction of Ag(II) compared to Cu(II), follows the trend seen in condensed phase chemistry as represented, for example, by the standard reduction potentials for the metals concerned,<sup>25,26</sup> which in turn is associated with the significantly lower free energy of solvation of Ag(II) compared with Cu(II).<sup>26</sup>

It is possible that the marked change in behavior seen for the silver(II) complexes as a function of size, is associated

with a switch in electronic transition on going from the first to the second solvation shell. Thus, in the second shell present in  $[\text{Ag}(\text{pyridine})_{6,7}]^{2+}$ , the reduced polarizing influence of the positive charge could lead to pyridine being excited to the  $S_1(n\pi^*)$  state. At  $\sim 280$  nm the  $S_1(n\pi^*)$  absorption coefficient for neutral pyridine in solution is a factor of  $\sim 100$  larger than that of the  $S_2(\pi\pi^*)$  transition;<sup>18</sup> therefore, the increased magnitude of the former could compensate for the smaller numbers of molecules occupying a second shell. The data presented for  $[\text{Ag}(\text{pyridine})_5]^{2+}$  could be seen as representing a transition between the two patterns of behavior: with charge transfer coming from  $S_2(\pi\pi^*)$  excitation and leading to the most stable Ag(I) arrangement,<sup>12</sup> and the loss of neutral pyridine resulting from  $S_1(n\pi^*)$  excitation and giving the most stable doubly charged configuration.<sup>9,23,24</sup> Such a switch would not be seen in condensed phase spectra because traditional Ag(II) complexes never contain more than four pyridine ligands.<sup>23,24</sup>

These preliminary experiments demonstrate the potential for spectroscopic/charge transfer studies on size-selected multiply charged metal–ligand complexes, with the differences seen here between Cu(II) and Ag(II) equating with their behavior in the condensed phase. The results also provided very strong support for an assumption adopted to interpret data on the relative intensities of  $[\text{M},\text{L}_n]^{m+}$  complexes;<sup>3,7–9</sup> namely, that large excited ions preferentially fragment down to the most stable structure. Such a correlation between fragmentation pattern and stability on the part of the ions, removes any ambiguity regarding the method of cluster preparation and the influence it may have on a typical mass spectrum.<sup>27</sup>

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