

Novel metal cluster complexes synthesized by matrix deposition of mass-selected clusters

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Abstract. Metal complexes produced by depositing size selected Fe and Ag cluster cations in N_2 and O_2 matrices respectively are studied by infrared spectroscopy. Unknown species such as $Fe(N_2)_x$, $Fe_3(N_2)_x$ and $Ag_3(O_2)_x$ are observed. The IR spectra of Ag^+ , Ag_2^+ and Ag_9^+ in excess O_2 indicate that no complexes involving molecular oxygen are formed. However, the strong silver cluster UV-visible absorptions detected in Ar matrices disappear in the oxygen matrices, suggesting that silver-oxygen complexes are formed with dissociated oxygen.

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Introduction

Matrix isolation has been widely used in order to synthesize and characterize a large number of novel metal complexes. Commonly, the evaporated metal is co-condensed with the gas host onto a cold substrate, forming the sample. While this technique allows the production and identification of new mononuclear binary complexes, the lack of metal cluster size selection makes it exceedingly difficult to study polynuclear metal species [1]. In order to overcome this problem, we have developed an experiment which allows us to directly synthesize polynuclear metal complexes by co-depositing size-selected metal cluster ions with excess ligand. Infrared spectroscopy in the region of the ligand vibrational modes and UV-visible absorption are used to characterize the resulting matrix. The study of iron carbonyls obtained by co-depositing Fe_x^+ ($x=1-3$) with CO showed that direct cluster/ligand deposition can lead to novel complexes with structures differing from ones with the same nuclearity but produced by conventional techniques [2]. Very recently, we were able to synthesize tetra-iron carbonyls as well as $Ag_x(CO)_y$ ($x=1-3$) complexes [3]

In this paper, the IR spectra of Fe_x^+ ($x=1-3$) deposited in N_2 , and Ag_x^+ ($x=1, 2, 3, 9$) deposited in O_2 are presented. The Ag- O_2 system is particularly interesting due to its industrial significance. Silver powder is extensively used as a

catalyst in the oxidation of ethylene to ethylene oxide providing the feedstock chemical for the production of ethylene glycol [4]. The use of other metals leads to undesired total combustion. Whether ethylene reacts with O_2 or with oxygen atoms at the silver surface remains in some aspects unclear. So it is important, at first, to know which form oxygen prefers when it adsorbs on a silver surface. To our knowledge, no reaction has been detected between gas phase silver clusters and oxygen. In addition, it has been shown that gas phase silver cluster anions do not react with CO while they react weakly with O_2 [5]. Our results indicate that silver cluster cations react with O_2 to form compounds involving atomic rather than molecular oxygen, except in the case of Ag_3^+ .

Experimental

The experimental apparatus has been described previously [2, 6]. Briefly, cluster ions were sputtered from a metal target using an intense Ar ion beam (15 mA, 25 kV), mass-selected using a Wien filter, and co-deposited with the gas of interest on a cold cesium iodide window (< 25 K) under ultra-high vacuum conditions. Ions were neutralized with a low energy electron beam situated in the deposition area. However, the clusters are likely ionic during at least the initial reaction with the ligand. The ligand:metal ratio was kept close to $10^4 : 1$. For both metals, the cluster ion currents ranged between 2 and 20 nA at 20 eV of kinetic energy (common to all our deposits), measured in a 2 mm diameter spot. IR spectra were collected by passing the modulated beam of a 1 cm^{-1} resolution Fourier transform infrared spectrometer (Bomem MB-100, lower threshold at 650 cm^{-1}) through the sample onto an MCT detector. The infrared beam was focused at the sample by a 35 cm focal length mirror. For UV-visible spectroscopy, a D₂ or W light source followed by a single pass monochromator (Heath EU-700) produced monochromatic light, which was passed through the sample and focused onto a photomultiplier equipped with photon-counting. The absorption could be measured as a function of the vertical position across the deposit through a horizontal 2×8 mm slit. Peaks whose intensities correlated with the cluster beam profile were assumed to be related to species originating in

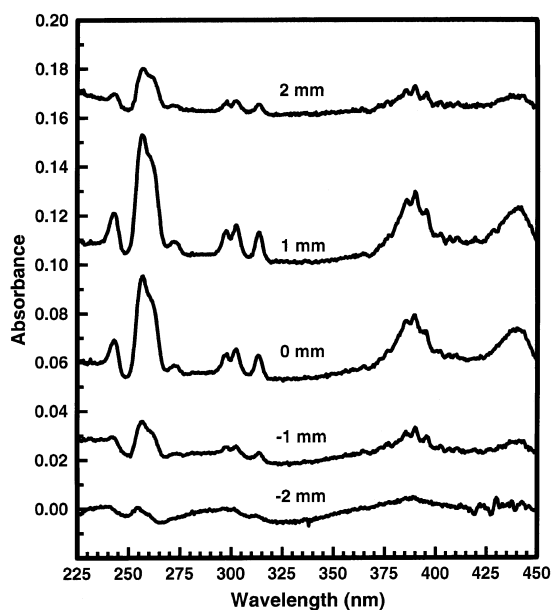


Fig. 1. Spatial profile of the UV absorption of 5 nA-hr Ag_2 deposited in an Ar matrix. Spectra are labeled with their position relative to the ion beam axis

the cluster beam. As an example, Fig. 1 presents five UV-visible absorption spectra of a sample obtained after the co-deposition of 5 nA-hr of Ag_2^+ with argon for different vertical positions, from which the beam profile can be deduced. The spatial profile of the cluster ion beam was roughly Gaussian, with a full width at half-maximum of approximately 3 mm. Spectra were further optimized by adjusting the horizontal position of a 2×8 mm vertical slit placed near the sample to restrict the light beam to a 2×2 mm region of the matrix containing complexes.

Iron in nitrogen

Figure 2 shows the IR spectra obtained after the co-deposition of Fe^+ , Fe_2^+ and Fe_3^+ with nitrogen. To our knowledge, only

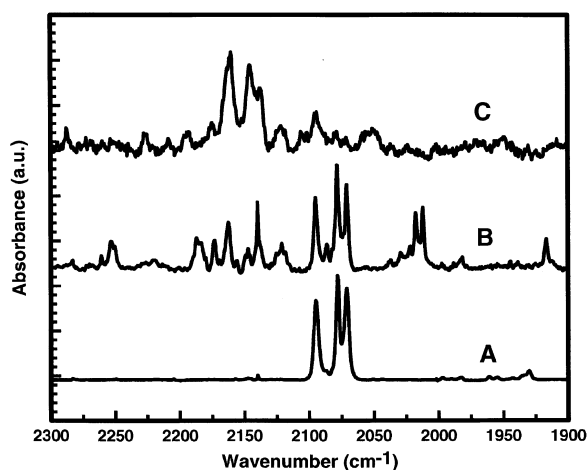


Fig. 2. Infrared absorbance of A) Fe, B) Fe_2 and C) Fe_3 in N_2 matrices, from deposits of 12, 4 and 2.5 nA-hr respectively. A baseline has been subtracted

Table 1. Infrared frequencies (cm^{-1}) of Fe/N_2 , Fe_2/N_2 and Fe_3/N_2 complexes

Complex	Observed IR frequencies in N_2 matrices
Fe/N_2	2095 s, 2088 sh, 2087 s 2071 s
Fe_2/N_2	2253m, 2221w, 2186m, 2173m, 2162s, 2148w, 2140m, 2121m,br, 2088m, 2037w, 2029w, 2022w, 2018s, 2012s, 1982w, 1917m
Fe_3/N_2	2288w, 2227w, 2209w, 2194w, 2175w, 2160s, 2146s, 2138m, 2121w, 2095m, 2050m,br

Barrett and Montano reported the observation of a di-iron nitrogen binary compound [7]. They recorded the Mössbauer and IR spectra of evaporated iron in nitrogen matrices at different Fe concentrations. While they assigned the IR peaks observed at high concentration to di-iron nitrogen complexes, there was no evidence of mono or tri-iron compounds. Attempts by Moskovits et al. to form Fe/N_2 complexes by evaporation of Fe into N_2 matrices also found no reaction [8]. In contrast, our spectra indicate clearly that mono- and tri-iron complexes are formed. The characteristic $\text{Fe}(\text{N}_2)_x$ spectrum (three peaks at 2095, 2078 and 1971 cm^{-1} in Fig. 2a) is also present in spectra of the dimer and trimer deposits, indicating that some fragmentation occurs during deposition. All of the other peaks in Fig. 2b (see Table 1) are attributed to di-iron nitrogen compounds and agree fairly with the previously reported spectrum [7]. The fact that agreement is not complete could be due to the presence of multiple di-iron compounds and/or multiple sites. The number of peaks in the spectrum also seems high for them to be attributable to a single species in a single site. In Fig. 2c, three main absorption peaks centered near 2160, 2146 and 2138 cm^{-1} and numerous weaker features (see Table 1) are assigned to tri-iron nitrogen complexes. Our observation of the formation of an $\text{Fe}(\text{N}_2)_x$ complex where earlier attempts showed no reaction is likely due to the ionic nature of the Fe precursor. Fe^+ has an open s shell $3d^6 4s^1$ ground state configuration. The cation is, therefore, already fully prepared to form the σ orbital responsible for the major portion of the bond in Fe/N_2 complexes. The neutral atom has a $3d^7 4s^2$ ground state and must be energetically promoted to reach the $3d^7 4s^1$ state favourable to σ bonding. Previous studies involved the neutral atom. The structure of the complex formed between the single Fe atom and N_2 can be partly clarified by using mixed isotope deposits. These will be reported elsewhere.

Silver in oxygen

Figure 3 displays the IR spectra of two different samples prepared by the co-deposition of Ag^+ and Ag_3^+ with oxygen. The sharp peak common to both spectra centered at 1038 cm^{-1} is assigned to the asymmetric stretching frequency (ν_3) of the ozone molecule. A weak feature at 702 cm^{-1} , seen in deposits of Si_2^+ in O_2 , corresponds to the O_3 bend frequency (ν_2) of O_3 . These values agree well with previous IR studies of ozone in solid oxygen (1050 and 704 cm^{-1}) and in gas phase (1043 and 705 cm^{-1}) [9]. Only the ozone peaks are observed after the deposition of Ag_2^+ , Ag_9^+ and Si_2^+ in oxygen matrices. The 1038 cm^{-1} band intensity was diminished but

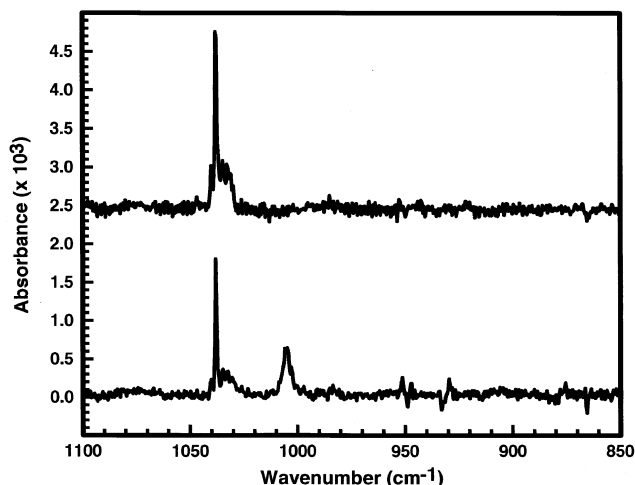


Fig. 3. Infrared absorbance of Ag (upper trace) and Ag₃ in O₂ matrices, from deposits of 5 and 3 nA-hr respectively. A baseline has been subtracted

still existent far from the beam center. Spectra from deposits made with the ion beam blocked also showed a weak ozone peak, indicating that ozone is produced by both the low energy electron flux and, more strongly, by the ion beam. It is not clear whether ozone is formed directly from oxygen due to the energy involved during the ion impact or is a product of a reaction such as $\text{Ag}_x + 2\text{O}_2 \rightarrow \text{Ag}_x\text{O} + \text{O}_3$. However, the ozone signal was three times less intense than the signal from an equivalent silicon deposition, suggesting that the ozone is a reaction product.

Another IR absorption band centered at 1005 cm^{-1} is observed after the deposition of Ag₃⁺. Because it correlates with the beam profile and was not detected in any other deposits, we assign this peak to Ag₃(O₂)_x. This is the only case where we observed the formation of a silver complex containing an O₂ ligand. In contrast, McIntosh and Ozin [10] assigned IR peaks of samples prepared by the co-condensation of Ag atoms and various O₂/Ar mixtures, to Ag(O₂) and Ag(O₂)₂. They also assigned an UV absorption band near 280 nm to those species, while we did not observe any UV-visible absorption in our Ag⁺ deposits. In Fig. 4, we present the UV absorption spectra obtained after the deposition of Ag₉⁺ in O₂ and Ar matrices. They show that the known Ag₉ absorption band visible in the Ar matrix [11] completely vanished in O₂. The narrow peak in the Ar spectrum centered at 340 nm corresponds to the heptamer absorption. The presence of Ag₇ in the matrix is not due to fragmentation but is a consequence of the resolution and setting of the mass filter, which was not completely optimized for Ag₉. Because the samples prepared with Ag and Ag₂ also do not present any UV or visible absorption, we conclude that O₂ reacts dissociatively with Ag₁⁺, Ag₂⁺ and Ag₉⁺ (and most likely with Ag₇⁺ too). In the case of Ag₉ (and Ag₇), the s-electrons that contribute to the plasmon-like absorptions presumably become involved in covalent bonding with oxygen atoms, and are no longer available for the plasmon resonance. The deposition of Ag⁺

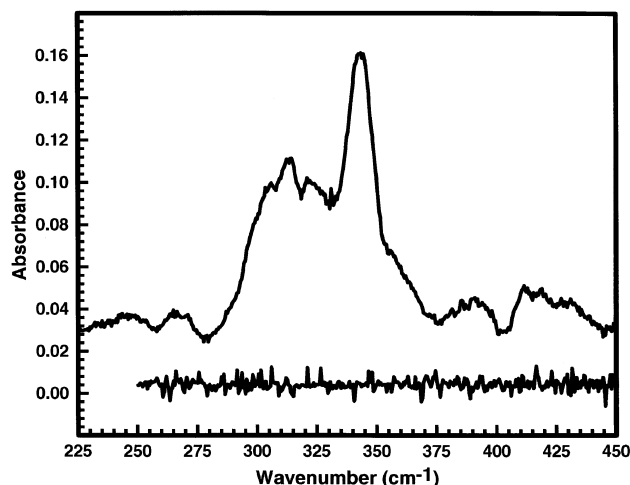


Fig. 4. UV absorption spectra of Ag₉ deposited in O₂ (lower trace) and Ar. In both cases a very broad background has been subtracted

in O₂ matrix most likely forms AgO which, although it has a visible fluorescence, has no UV-visible absorption [12]. Unfortunately, the vibrational frequency of AgO (490 cm^{-1} [12]) is below the threshold of the MCT detector so the AgO product could not be confirmed.

In summary, we have employed the technique of co-depositing size-selected metal cluster ions with excess ligand to synthesize a number of previously unknown metal complexes. It is clear that the method is particularly useful studying polynuclear complexes that are inaccessible through more conventional means.

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