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Ion-Molecule Reactions of Organic Molecules with Noble Metal Atoms in Superfluid Helium Droplets

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Abstract. Superfluid helium droplets (HeDs) provide a unique environment for the study of physical and chemical phenomena at a very low temperature. Properties of HeDs include the very low temperature (0.37 K), superfluidity and the ability to capture a wide variety of atoms and molecules. Subsequently, the molecules isolated in HeDs can be studied by mass spectrometry and/or spectroscopy. In this work, dissociative ion-molecule reactions of metal-organic complexes formed in superfluid HeDs are reported. Two organic molecules, 1-pentanol and 1,9-decadiene, and two noble metals, gold (Au) and silver (Ag), were employed to form binary metal-organic complexes by sequential addition of organic molecules and metal atoms to superfluid HeDs. The resulting complexes were then investigated by mass spectrometry. Electron impact of a doped HeDs first creates a He^+ ion, which ionizes the embedded molecules through resonance charge transfer. This highly energetic process delivers excess energy to the molecular clusters, leading to dissociative ion-molecule reactions. The mass spectra show softening effects and caging effects induced by the superfluid helium for both 1-pentanol and 1,9-decadiene, and the co-addition of Ag or Au has been found to have minor influence to the fragmentation patterns, except for the 1,9-decadiene-Au complex. This is attributed to the different ionization energy of the selected molecules and metals, which influences the overall energy delivered to the organic molecules studied and thus the degree of fragmentation.

Keywords : Binary Complex, Ion-molecule reaction, Mass Spectrometry, Superfluid Helium Droplets

INTRODUCTION

Helium droplets (HeDs) are large clusters of superfluid helium typically composed of 10^3 - 10^{11} helium atoms [1,2,3]. Having remarkable properties as a superfluid, HeDs provide a means to study molecules and molecular clusters in isolated nanoreactors. Due to the superfluidity and the very low steady-state temperature, HeDs have an ultrahigh cooling rate for the species captured, *i.e.*, by evaporation of weakly bound helium atoms. Doping of single or multiple atoms/molecules to a droplet is possible, which can be achieved by collision(s) between the droplet and gas-phase atoms/molecules. This process is highly “sticky”, with a near unity pickup probability upon each collision event [4]. When different types of molecules/atoms are added to HeDs, binary clusters can be obtained, which can be investigated, for example, by mass spectrometry and spectroscopy [5].

Electron-impact (EI) mass spectrometry is one of the most commonly used methods for studying the molecules or clusters embedded in HeDs. The ionization process starts with the creation of a He^+ ion near the surface of the droplet, which then transfer its charge to the dopants *via* a charge transfer process proposed by Atkins [6]. If the He^+ ion reaches an impurity after a small number of hops, it can transfer its charge to the dopant [7,8] resulting in ionization and subsequent ion-molecule reactions due to the large ionization energy of the helium atom. Otherwise, it may terminate by the formation of He_n^+ ions by self-trapping, predominantly leading to the formation of He_2^+ . A combination of experimental and associated theoretical model showed that the number of hops is about 10 before

self-trapping occurs [7, 8, 9]. The charge hopping process ceases as soon as the He^+ ion transfers its charge to the dopant or localizes to form a He_n^+ ($n \geq 2$) cluster ion [7].

Due to the low temperature and rapid cooling of superfluid helium, atoms/molecules can no longer escape once being captured by the droplet. The superfluidity of helium then allows the dopant to migrate in the droplets and form clusters when more than one molecule/atom is added to the droplet. This eases the formation of metal-organic complexes, which involves relatively cold molecules and hot metal atoms produced by oven evaporation. By this route, Cheng *et al.* formed metal-organic clusters containing 5,10,15,20-tetra(4-pyridyl)porphyrin (H2TPyP) and Au, and investigated the ion-molecule reactions initiated by electron impact [10]. The Au atom was found to have diverse effect to the fragments of the H2TPyP molecule. For example, it changes the relative abundances of methylpyridine; but only has little influence to other fragments like pyridine and pyrrole groups. Here we formed metal-organic complexes using superfluid HeDs by the co-addition of noble metals, Au or Ag, and organic molecules, 1-pentanol and 1,9-decadiene to HeDs, and investigated ion-molecule reactions by use of electron impact ionization mass spectrometry. We also studied the mass spectra of organic molecules in HeDs for comparison. By this means we intend to learn how the metal atom added will affect the fragmentation of organic molecules in superfluid HeDs.

EXPERIMENTAL METHOD

This work employed an ultra-high vacuum helium nanodroplet apparatus consisting of three chambers: the source chamber, pickup chambers and the analysis chamber, as being detailed previously [11,12]. Briefly, HeDs are formed by supersonic expansion of pre-cooled high purity helium gas through a 5 μm pinhole nozzle, which then pass through a 0.5 mm skimmer and form a collimated HeDs beam. The helium source temperature was maintained at 10.5 K and the stagnation pressure was 15 bar, producing droplets composed of 10^3 - 10^4 helium atoms. In the pickup region three pickup cells were equipped: the first was the gas cell for doping organic molecules, the second and the third were resistively heated ovens for the evaporation of gold and silver, respectively. Pentanol/decadiene was delivered to the first gas pickup cell through a needle valve. Both chemicals were purchased from Sigma Aldrich (with stated purities of >98%) and were thoroughly degassed before use. To study the ion-molecule reaction of monomers, the needle valve was tuned so the majority of HeDs contained no more than one pentanol/decadiene molecule. The droplet then traveled to another oven where it acquired a metal atom. The oven temperature was carefully controlled so that on average each droplet was doped with a single Au or Ag atom. Further downstream a quadrupole mass spectrometer (Max-4000HT, Extrel, which operates up to m/z 4000), equipped with an electron ionization source operating at 70 eV, was used to measure mass spectra of the doped droplets.

RESULTS AND DISCUSSION

Ion-Molecule Reactions of 1-pentanol-metal complexes

To see the influence of noble metal atoms to the fragmentation pattern of 1-pentanol, we first look at the mass spectrum of 1-pentanol without the addition of the Au atom and the gas phase mass spectrum. As seen in Figure 1, the helium droplets significantly influence the fragmentation patterns of 1-pentanol. In the gas phase spectrum, the m/z 27, 29 and 31 channels (marked as A, B and C, respectively) are the most intense products whereas in the HeDs mass spectrum, the relative intensities of these peaks were altered. The m/z 27 and 31 peaks have much reduced branching ratios compared with the m/z 29 peak, and some other peaks also emerged as prominent products in the mass spectrum, *e.g.*, peaks D, E and F, in addition to the parent ion channel M and the hydrogen-loss channel. The observation of parent ion in mass spectrum of doped helium suggests that the helium droplet has softened the ionization of 1-pentanol. The peaks A, B and C can be assigned to vinyl cation, ethyl cation and protonated formaldehyde. Moreover, the m/z 42 peak, which is notable in the gas phase spectrum and corresponds to the loss of both H_2O and C_2H_4 , suffers a major decline in relative abundance in the helium droplet mass spectrum while the m/z 43 peak gains in intensities.

The energetics of the ionization is clearly one of the major factors influencing the fragmentation patterns. In droplets of any significant size, the most likely initial ionization event will be the removal of an electron from a helium atom near the surface of the droplet to create a He^+ ion, which delivers a total energy of 24.5 eV to the doped

molecules if they meet. In contrast, the energy of direct ionization by electron impact is much higher, namely, 70 eV. Hence, through charge transfer ionization less energy will be delivered to the molecule. In addition, HeDs might have other effects that can also influence the fragmentation pathways. For instance, the observation of the hydrogen-loss channel is likely a caging effect [13,14,15], where small fragments like hydrogen atom can gain sufficient kinetic energy and escape from the droplets but heavy fragments cannot.

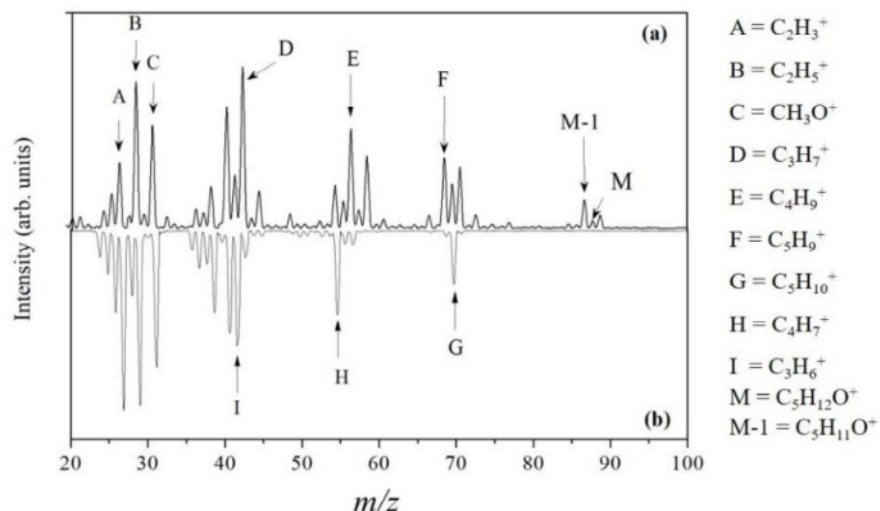


FIGURE 1. Comparison between the mass spectra of 1-pentanol: (a) doped in HeDs; (b) in the gas phase. The assignment of these peaks is listed on the right.

We now compare the mass spectrum of 1-pentanol in HeDs with that of the 1-pentanol-Au and 1-pentanol-Ag complexes at the low mass region. As seen in Figure 2, both sets of mass spectra are similar, and the addition of Au or Ag has little effect on the fragmentation pattern of 1-pentanol. The relative intensity of the peaks slightly changed and there is no clear evidence of one fragmentation pathway becoming more favored than any others when Ag/Au was co-added. This can be interpreted by the ionization energy of Ag and Au, both being lower than 1-pentanol. In this case both Ag and Au have a poor buffer effect to the dissociative ion-molecule reactions of the molecule. If the charge of He^+ is transferred to Au or Ag atom, in the subsequent reactions one expects no fragments from 1-pentanol as Ag^+ and Au^+ ions cannot ionize 1-pentanol. On the other hand, if the charge is transferred to 1-pentanol, Ag and Au can only affect the fragmentation pattern due to the very weak interaction between 1-pentanol and Ag/Au, which, as indicated by the mass spectra, is a minor effect.

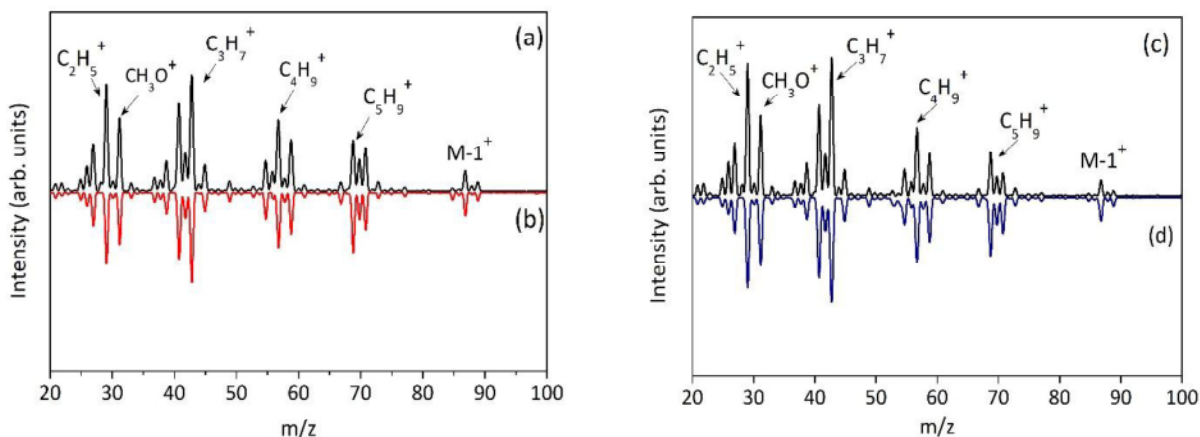


FIGURE 2. Comparison between 1-pentanol and 1-pentanol-metal complexes in HeDs.

(a)–(b) binary complex pentanol-Au: (a) 1-pentanol; (b) 1-pentanol-Au;
(c)–(d) binary complex pentanol-Ag: (c) 1-pentanol; (d) 1-pentanol-Ag

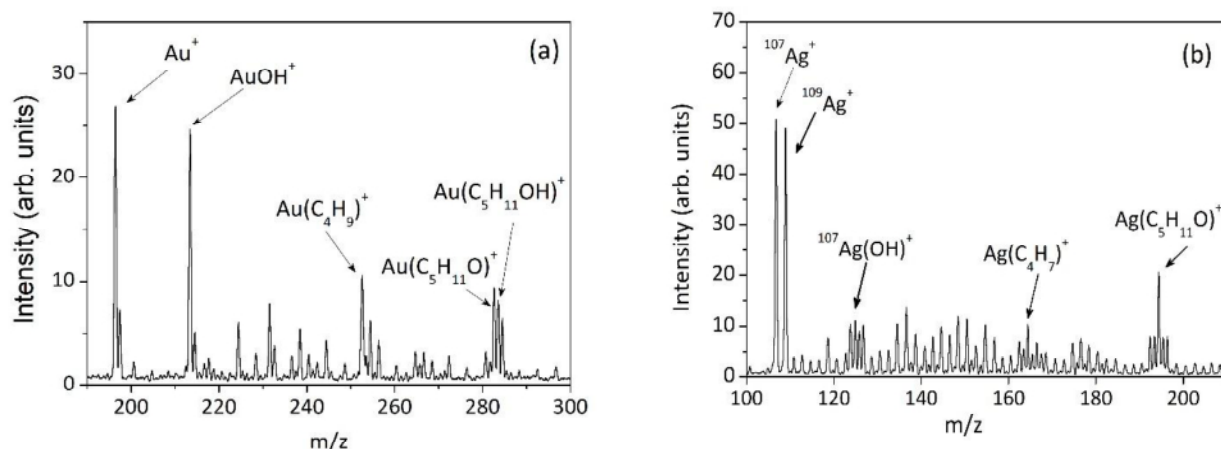


FIGURE 3. HeDs mass spectra of binary complex containing 1-pentanol and a single metal atom.
(a) 1-pentanol-Au: (b) 1-pentanol-Ag.

Figure 3 shows the mass spectra of 1-pentanol-Au and 1-pentanol-Ag at higher mass region, with fragments of 1-pentanol attached to Au and Ag, respectively. The major fragments in 1-pentanol-Au complex are m/z 253, 283 and 284 peaks. By subtracting the mass of Au from each of the peaks, the mass of the 1-pentanol fragments can be obtained, giving rise to m/z of 57, 87 and 88, respectively. The m/z 87 and 88 peaks are the M^+ and $M-1^+$ peaks of 1-pentanol, respectively; while the m/z 57 peak corresponds to the $C_4H_9^+$ fragment. For 1-pentanol-Ag complex, we observed similar fragments attached to Ag, as seen in Figure 3(b). The intensity of all the peaks in the m/z 20 - 100 range was reduced by 24-25% relative to the intensity in the pure pentanol spectrum. In both spectra, the reduction in the peak intensity in the m/z 20 - 100 range was equal to the sum of the $(Au/Ag-C_5H_{11}OH)^+$, $(Au/Ag-C_5H_{11}O)^+$ and $(Au/Ag-C_4H_9)^+$ peak intensities, suggesting that these fragments derived from the dissociation of 1-pentanol upon charge transfer ionization, which partially attached to Au or Ag.

Ion-Molecule Reactions of 1,9-decadiene-metal complexes

Figure 4 compares the gas phase mass spectrum of 1,9-decadiene with that in HeDs. The major fragment ions are very similar in two spectra but the intensities have been altered, in particular, the relative intensities of the A and B peaks in HeDs are significantly weaker than the gas-phase spectrum. In addition, the spectrum of doped HeDs also shows parent ions and the hydrogen-loss channel, which do not appear in the gas phase mass spectrum. Similar to 1-pentanol, the observation of parent ions suggests a certain degree of softening by the HeDs, presumably due to the lower total energy delivered to the system; while the hydrogen-loss channel can be interpreted by the caging effect.

The addition of Ag and Au has different effects to the ion-molecule reactions of 1,9-decadiene. When Au was co-added to HeDs with 1,9-decadiene, it significantly reduced the fragments of 1,9-decadiene (see Figure 5). In particular, the low mass fragments, e.g. $C_2H_3^+$ and $C_3H_3^+$, have been significantly reduced relative to other peaks. On contrary, the mass spectrum of 1,9-decadiene-Ag complex shows no obvious difference to the mass spectrum of 1,9-decadiene. These observations strongly support our interpretation to the mass spectra of 1-pentanol-metal complexes based on relative ionization energies. Using density functional theory (DFT) calculations at B3LYP/6-311G(d,p) level of theory, we found that the ionization energy of 1,9-decadiene is 8.6 eV, which is higher than the ionization energy of Ag (7.57 eV) [16] and lower than that of Au (9.22 eV) [17]. As the ionization energy of Ag is lower, it has negligible influence on the ion-molecule reactions of the two molecules, as observed in this work. For Au, its ionization energy is lower than 1-pentanol but is higher than 1,9-decadiene. As a result, in the secondary ionization process when the charge is transferred from Au to 1,9-decadiene, the total energy delivered to the molecule is significantly reduced, resulting in significantly reduced fragmentation of the molecule.

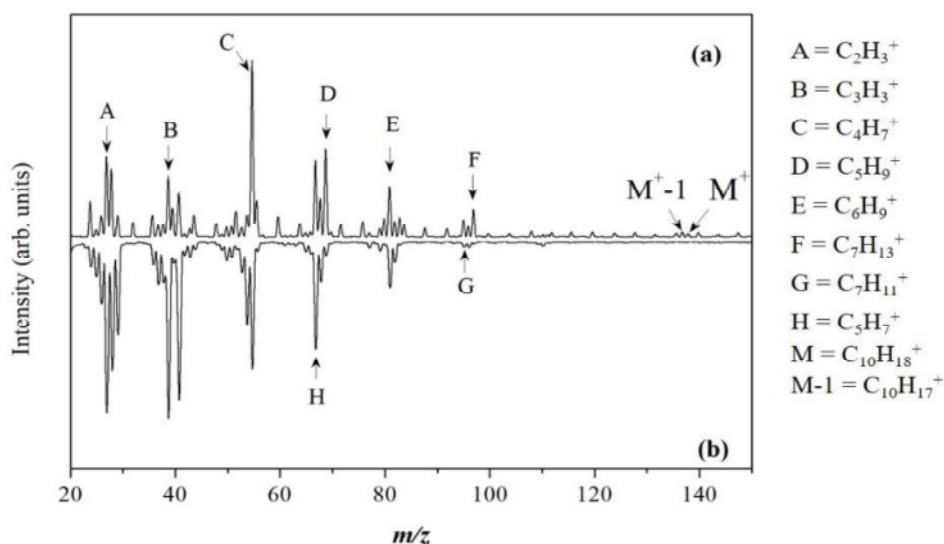


FIGURE 4. Comparison between the mass spectra of 1,9-decadiene (a) doped in HeDs; (b) in gas phase.

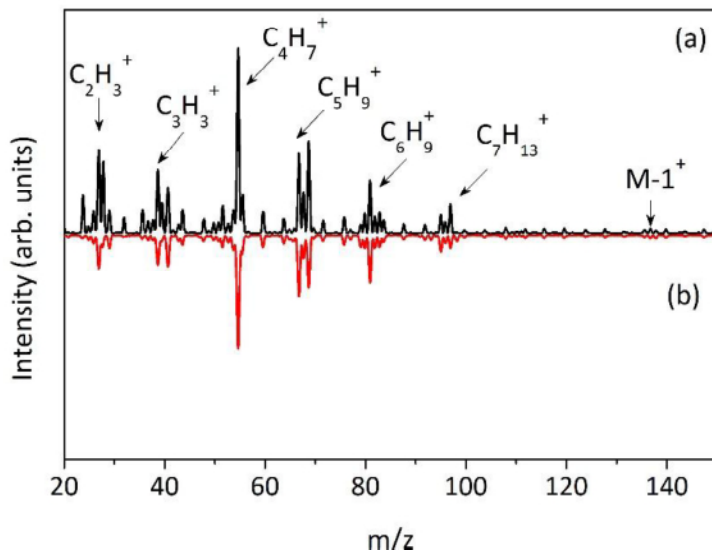


FIGURE 5. Mass spectra of doped HeDs containing (a) 1,9-decadiene, and (b) 1,9-decadiene-Au complex.

CONCLUSION

In this work we investigated the ion-molecule reactions in doped HeDs containing an organic molecule and a noble metal atom initiated by charge transfer ionization. Without the addition of Ag and Au, the mass spectra of doped HeDs clearly showed softening effect for both 1-pentanol and 1,9-decadiene. We also observed a hydrogen-loss channel in both cases, which has been interpreted by the caging effect. The mass spectra of binary clusters formed in HeDs, including 1-pentanol-Au, 1-pentanol-Ag and 1,9-decadiene-Ag, showed negligible difference to those of 1-pentanol and 1,9-decadiene, but the mass spectrum of 1,9-decadiene-Au has been found drastically different from that of decadiene. These provoke an important mechanism related to the relative ionization energy of

metals and organic molecules: the metal atom will have a strong buffer effect to the ion-molecule reactions if it has higher ionization energy than that of organic molecules.

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