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Cluster/Surface Interactions and Cluster/Mat rix Dep osition

by

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CLUSTER/SURFACE INTERACTIONS AND CLUSTER/MATRIX DEPOSITION

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ABSTRACT

This paper reports the most recent results from the cluster chemistry program at the Naval Research Laboratory, in which our efforts in the characterization of gas-phase cluster properties have been extended to studies of condensed-phase species. First, in an attempt to investigate the fundamental interactions between mass-selected cluster ions and surfaces, two tandem mass spectrometers were constructed or modified, and the results of the initial experiments will be discussed. The emphasis will be on illustrating the general utility of ion/surface collisions to study fragmentations, reactions, and deposition. Second, clusters were deposited into a matrix in order to perform spectroscopic analyses. The initial experiments have been directed at optimization of the techniques. Finally, recent measurement of the ionization potentials of large carbon clusters will be reported. These results are especially significant because of the new developments in large-scale production, isolation, and characterization of these species.

INTRODUCTION

In the past few years gas-phase clusters have been studied extensively; however, relatively less research has been focused on similar, condensed-phase species. Such studies are crucial to obtaining a detailed understanding of how some of the interesting gas-phase clusters with unique properties will make the transition to the condensed phase. Fundamental knowledge of the structures and properties of clusters deposited on a surface, or in a matrix is necessary in order to enhance the potential of clusters as film precursors, surface modifiers, or new materials. The most recent objective of the cluster chemistry program at the Naval Research Laboratory, which has been active for more than 10 years, is to extend the investigations of gas-phase cluster structures and chemistry to the characterization of the same properties of clusters that have been transferred from the gas phase. This new direction for our program has two components: (1) investigation of the fundamental interactions between clusters and a surface, and (2) spectroscopic analysis of clusters deposited into a matrix. The emphasis of this report is on the techniques and information obtained from the ion/surface studies, and these results will be important in the design of the cluster/matrix deposition experiments. In addition, the continuing gas-phase experiments are directed, most recently, at understanding the reasons for the special nature of anomalously abundant clusters, such as the large carbon cluster ions, C_{2n} and C_{2n+1} . These studies, which have focused on measurement of the ionization potentials and reactivities of these species, have yielded new insights that are especially important due to recent developments in this area.

EXPERIMENTAL

The studies on ion/surface collision-induced interactions are performed in two different tandem mass spectrometers. One of these, a specially-constructed tandem time-of-flight mass spectrometer based on the design published by Schey, *et al.* [1], is shown in Figure 1. Ions are formed by electron ionization (EI) of volatile precursor compounds or by direct laser vaporization (DLV) of solid target materials. The ions are extracted from the source region and pass through a field-free region where they separate due to different velocities. One ion mass or size is selected and allowed to collide with a stainless steel surface at the end of the flight tube. The ions that result from the collision are extracted and detected with a second time-of-flight mass analyzer, which is positioned at a 90° angle with respect to the first analyzer.

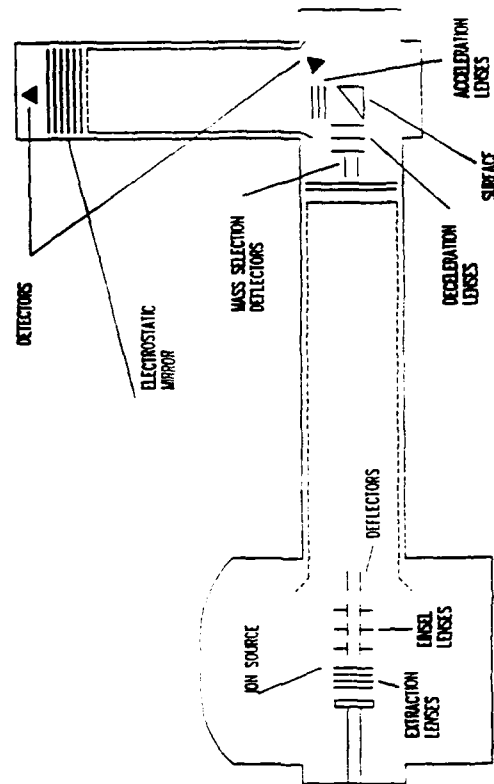


Figure 1. Diagram of the tandem time-of-flight mass spectrometer

Ion/surface collisions are performed also in a Finnigan TSQ-70 triple quadrupole mass spectrometer. In this linear instrument, ions that are formed by EI, chemical ionization (CI), or particle bombardment are extracted from the source into the first quadrupole mass filter (Q1). One mass-to-charge ratio ion is selected with Q1 and deflected onto a stainless steel surface. The ions resulting from this collision are extracted into an RF-only quadrupole (Q2) ion guide and mass analyzed with the subsequent quadrupole mass filter (Q3). The results from ion/surface collisions on this instrument are compared with those from studies using a tandem quadrupole instrument (at VCI), which has a 90° geometry with the surface oriented at a 45° angle with respect to both ion flight axes. These studies allow evaluation of the effects of collision energy, collision angle, surface composition, and instrument geometry.

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In the second phase of these new efforts, clusters that are produced by direct laser vaporization are deposited into a frozen rare gas matrix. Spectroscopic analysis can be performed using laser-induced fluorescence or Fourier transform infrared spectroscopy. The first experiments were directed at optimization of carbon cluster deposition so that all clusters that were vaporized from the graphite rod were deposited into the argon matrix. This work will not be discussed here; yet, the intent is to study mass-selected clusters.

Finally, the further characterization of the properties of the anomalously abundant large carbon clusters was performed in a Fourier transform mass spectrometer (FTMS). The method of cluster ion production and analysis have been described [2]. In this study, a carbon cluster ion is size (mass) selected and allowed to react with a gas-phase species of known ionization potential. The presence or absence of the possible charge-transfer reaction product ion is indicative of the relative ionization potentials. In this manner, the ionization potentials of selected carbon clusters were determined.

RESULTS AND DISCUSSION

Ion/surface collisions

The objective of our initial ion/surface experiments was to demonstrate and investigate the processes that can occur using precursor ions of known structure and gas-phase chemistry. With this fundamental knowledge, the studies can be extended to more complicated, higher mass species. The processes that occur in a collision between the benzene radical cation, $C_6H_6^+$, and a surface were explored first. At collision energies of greater than approximately 10 eV the benzene molecular ion dissociates with the observation of fragment ions corresponding to characteristic losses of neutral C_2H_4 units. These benzene surface-induced dissociation (SID) mass spectra are similar to gas-phase collision-induced dissociation (CID) mass spectra, except for the collision energies at which the fragment ions appear. This aspect will be discussed further below. If the collision energy is less than 30 eV, ions are observed at mass-to-charge ratios greater than that of the precursor ion. The surface collision of the benzene molecular ion (m/z 78) yields ions at m/z 79 and 91. These species are produced by reactions between the benzene ion and adsorbates on the stainless steel surface, resulting in hydrogen atom pick up to yield m/z 79 and methyl abstraction with subsequent loss of H_2 to yield a net gain of 13 mass units for the m/z 91 product ion. It is clear that impurity adsorbates on the surface are involved because when this experiment is performed in the FTMS, with high vacuum conditions ($<10^{-9}$ Torr) and a clean surface, these addition reaction product ions are not observed. These results are in agreement with another benzene/surface study [3].

As mentioned, the laboratory-frame ion/surface collision energy required to observe a particular fragment ion is not the same energy as in gas-phase CID. This was demonstrated in a comparison of the CID and SID of tungsten hexacarbonyl ($W(CO)_6$). Figure 2 shows the plots of the fragment ion abundances, corresponding to successive losses of CO ligands, as a function of the laboratory-frame collision energy for (a) CID and (b) SID of $W(CO)_6^+$. It is evident that for the same collision energy the surface collision imparts a significantly greater amount of energy to the precursor ion. In addition, the surface collision results in deposition of a narrower internal energy distribution. These observations demonstrate the potential of ion/surface collisions for structural elucidation of high-mass ions, such as clusters or biomolecules.

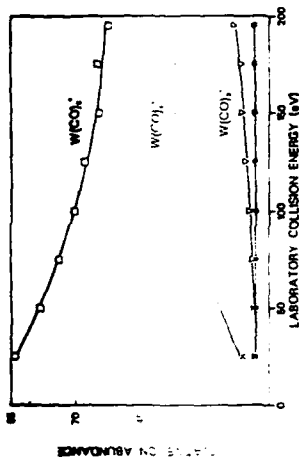


Figure 2a. CID of $W(CO)_6^+$

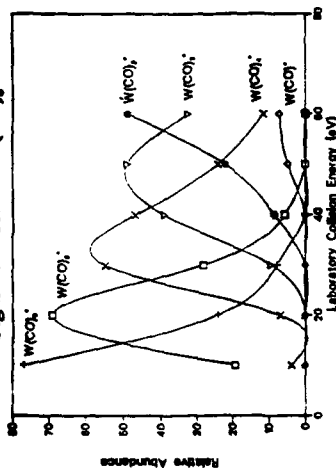


Figure 2b. SID of $W(CO)_6^+$

As promising as the previous results are, some aspects of ion/surface interactions require consideration and caution. The most significant potential problem is neutralization of the incoming precursor ion. In studies of alkali halide cluster ions, greater than approximately 5-10% of the precursor ion abundance can be collected as the undissociated ion or fragment ions after the surface collision. These species are known to have very low ionization potentials and, thus, the probability of charge transfer from the surface to the ion is low. However, in experiments with different precursor species, we have shown that neutralization can be significant. For example, when a 3-mass unit window containing the atomic ions of potassium (m/z 39 and 41) and argon (m/z 40) is focused onto the surface, only the two potassium isotope ions survive. The reason is the much higher ionization potential of argon (15.8 eV) versus that of potassium (4.3 eV), resulting in neutralization of Ar^+ but not K^+ . In a similar manner, when carbon cluster ions are collided with the surface only a small percentage of the precursor ion signal can be detected as fragment or undissociated ions. When C_{60}^+ is directed at a surface no fragmentation is observed at collision energies up to 100 eV, which is in agreement with another study [4]. However, when C_{60}^{2+} is collided with the surface only C_{60}^+ is observed as a result of a one-electron pick up from the surface. In addition to ion neutralization, sputtering of previously deposited materials can occur. For example, after studies of $Cs_2I_2^+$ /surface collisions, Ir_2^+ surface collisions yielded Cs^+ and Ir_2Cs^+ product ions. These observations illustrate the importance of the surface properties and suggest that the modification of the surface can significantly alter the observed fragmentations and reactions.

SUMMARY

These initial ion/surface interaction studies have illustrated some of the processes that can occur. The collision can impart large amounts of energy to the precursor ion with a relatively narrow distribution. This demonstrates a great potential for dissociating high-mass species to obtain information on structure and fragmentation energetics. In addition to dissociation, reactions of precursor ions resulting in abstraction of species from adsorbates on the surface. This could provide new information on cluster reactivity. Deposition of some species can occur along with subsequent sputtering. This can be a complication in interpreting the collision spectra or used to an advantage to produce a modified surface. The problem of precursor ion neutralization must be minimized or overcome to increase the applicability of the technique. This will involve studies with different types of surface materials or possibly thin films. In addition to yielding fundamental insights into ion/surface interactions, these experiments will provide important information for mass-selected cluster ion deposition for matrix isolation spectroscopy.

The recent experiments on the measurement of the ionization potentials of the large, abundant carbon clusters have revealed new information relating to their special nature. The C_{50} , C_{60} , and C_{70} species were found to have significantly higher ionization potentials than the neighboring clusters. The anomalously high abundances of these cluster ions are likely to arise from greater stability and unreactivity.

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Carbon cluster ionization potentials

It has been known for a long time that certain size carbon cluster ions have anomalously high abundances in mass spectra that are obtained in a variety of ways. In the high-mass region (C_n^+ , $n > 32$), the most well-known cluster is C_{50}^+ , with C_{60}^+ and C_{70}^+ also present in high abundances. Because these species are unreactive in the gas-phase and are difficult to dissociate, yielding fragment ions that are not structurally informative, another approach to gaining insight into the special stabilities was needed. The ionization potentials of these larger carbon clusters were determined to compare with those determined previously for the lower mass carbon clusters. The results of the charge exchange experiments in the FTMS are shown in the plot in Figure 3. It was found that C_{50} , C_{60} , and C_{70} have approximately the same ionization potential of 7.61 ± 0.1 eV, and that this is 0.5 eV higher than the ionization potentials of the neighboring clusters. This observation is in contrast to the situation with the smaller carbon clusters. In the lower mass region of the carbon cluster ion distribution the most abundant ions (e.g., C_2^+ , C_{11}^+ , C_{15}^+) arise from neutrals with ionization potentials that are lower than those of the neighboring, less abundant ions. These smaller carbon cluster ions are abundant because of a greater ionization efficiency while the anomalously high abundances of the larger carbon clusters with relatively higher ionization potentials may be due to a greater probability of survival in ion/molecule reactions. These studies were extended to investigate the relative reactivities of the larger carbon cluster ions and to the measurement of the second ionization potentials of these species. This work is especially significant given the recent developments in the large-scale production, isolation, and characterization of C_{50} and C_{70} and are reported in another paper in this publication.

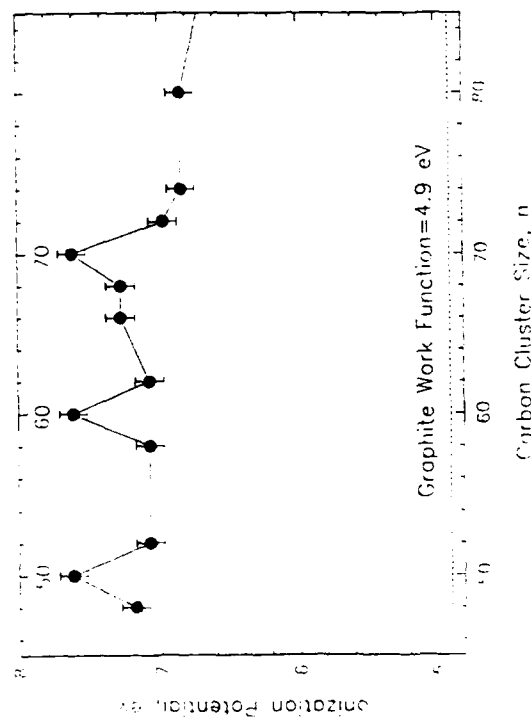


Figure 3. Carbon cluster ionization potential versus cluster size