Cluster/Surface Interactions and Cluster/Matrix Deposition

by

Mark M. Ross, John H. Callahan, Fred L. King
Vicki H. Wysocki, Stephan B.H. Bach, Herbert H. Nelson
Andrew P. Baronavski, and Stephen W. McElvany

Prepared for Publication
in the
Materials Research Society Symposium Proceedings

Virginia Commonwealth University
Department of Chemistry
Richmond, VA

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.
Best Available Copy
### Title and Subtitle
Cluster/Surface Interactions and Cluster/Matrix Deposition

### Authors

### Performing Organization Name(s) and Address(es)
Department of Chemistry
Virginia Commonwealth University
Richmond, VA 23284-2006

### Sponsor/Monitoring Agency Name(s) and Address(es)
Office of Naval Research
Chemistry Program
800 N. Quincy ST
Arlington, VA 22217

### Distribution/Availability Statement
Approved for public release

### Abstract (Maximum 200 words)
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.
### GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to stay within the lines to meet optical scanning requirements.

| Block 1. Agency Use Only (Leave blank). |
| Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year. |
| Block 3. Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88). |
| Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses. |
| Block 5. Funding Numbers. To include contract and grant numbers; may include program element numbers, project number(s), task number(s), and work unit number(s). Use the following labels: |
  - C - Contract
  - G - Grant
  - PE - Program
  - WU - Work Unit
  - Element Accession No. |
| Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s). |
| Block 7. Performing Organization Name(s) and Address(es). Self-explanatory. |
| Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report. |
| Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es) Self-explanatory. |
| Block 10. Sponsoring/Monitoring Agency Report Number. (if known) |
| Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of...; To be published in.... When a report is revised, include a statement whether the new report supersedes or supplements the older report. |

| Block 12a. Distribution/Availability Statement. Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR). |
| Block 12b. Distribution Code. |
| Block 13. Abstract. Include a brief (Maximum 200 words) factual summary of the most significant information contained in the report. |
| Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report. |
| Block 15. Number of Pages. Enter the total number of pages. |
| Block 16. Price Code. Enter appropriate price code (NTIS only). |
| Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited. |
CLUSTER/SURFACE INTERACTIONS AND CLUSTER/MATRIX DEPOSITION

MARK M. ROSS, JOHN H. CALLAHAN, FRED L. KING, VICKI H. WYSOCKI, STEPHAN B. BACH, HERBERT H. NELSON, ANDREW P. BARONAVSKI, and STEPHEN W. MCELVANY

Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375 5000.

1Department of Chemistry, West Virginia University, Morgantown, WV

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 intended 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 analyses of clusters deposited into a matrix. The emphasis of this report is on the technique 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_60 and C_{60+}. These studies, which have focused on measurement of the ionization potentials and reaction rates of these species, have yielded new insights that are especially important due to recent developments in this area.

EXPERIMENTAL

The studies on ion/surface collisions-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 Schley 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 of 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 VCU), 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.
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\textsubscript{6}H\textsubscript{5}\textsuperscript{+}, 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\textsubscript{6}H\textsubscript{4}H 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 adsorbrates on the stainless steel surface, resulting in hydrogen atom pick up to yield m/z 79 and methyl abstraction with subsequent loss of H\textsubscript{2} to yield a net gain of 13 mass units for the m/z 91 product ion. It is clear that impurity adsorbrates on the surface are involved because when this experiment is performed in the FTMS, with high vacuum conditions (<10\textsuperscript{-6} 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)\textsubscript{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)\textsubscript{6}\textsuperscript{+}. 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.

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 undisassociated 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\textsuperscript{+} but not K\textsuperscript{+}. In a similar manner, 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\textsubscript{60}\textsuperscript{+} 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\textsubscript{60}\textsuperscript{+} is colliding with the surface only C\textsubscript{60}\textsuperscript{+} 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\textsuperscript{+}/surface collisions, In\textsuperscript{+}, surface collisions yielded Cs\textsuperscript{+} and In,Cs\textsuperscript{+} 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.
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 \( \text{C}_n^+ \), with \( n \geq 42 \), also present in high abundances. Because these species are unreactive in the gas-phase and 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 couple 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 \( \text{C}_{20} \), \( \text{C}_{30} \), and \( \text{C}_{40} \) have approximately the same ionization potential of 7.61 \pm 0.01 \text{ eV} \), and that this is 0.5 \text{ 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., \( \text{C}_{22}^+ \), \( \text{C}_{24}^+ \), \( \text{C}_{26}^+ \)) 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 \( \text{C}_{24} \) and \( \text{C}_{30} \) and are reported in another paper in this publication.

![Graphite Work Function=4.9 eV](image)

**Figure 3.** Carbon cluster ionization potential versus cluster size

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 also, with subsequent sputtering. This can be a complication in interpreting the collision spectra or used to an advantage to probe 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 \( \text{C}_{20} \), \( \text{C}_{30} \), and \( \text{C}_{40} \) 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.

REFERENCES