Desorption Mass Spectrometry

Are SIMS and FAB the Same?

EDITED BY

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Are SIMS and FAB the Same?

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3M

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FOREWORD

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PREFACE

Mass SPECTROMETRIC INSTRUMENTATION and the capabilities for analysis of organic and organometallic molecules have undergone revolutionary advances in the last 3 years. Perhaps the most notable advances are in the area of volatilization and ionization of samples. In 1981, a new ion source was developed for a conventional high-resolution magnetic mass spectrometer that allowed the chemist for the first time to analyze organic compounds that were ionic, nonvolatile, or thermally unstable. This ion source used a fast atom beam to generate the organic ions. Tremendous growth has occurred in the use of the fast atom bombardment (FAB) source in combination with conventional mass spectrometers, both in academic research and in industrial problem solving.

The technique of FAB mass spectrometry (FABMS) has many similarities to that of secondary ion mass spectrometry (SIMS). The basic designs of the ion sources are similar, and these sources may share a common mode of generating ions. However, many researchers using FABMS consider their work to be original discoveries and disregard a wealth of knowledge in the field of the surface scientist. The SIMS method is significantly ahead of FAB in its development. Those doing FABMS have much to learn from SIMS studies. This condition of two analytical techniques advancing down parallel paths without any interaction slows the progress in both fields and, more importantly, prevents full utilization of these techniques.

The symposium upon which this book is based was held to encourage an open dialogue between researchers in the fields of SIMS and FABMS. The intent of the symposium and this book is to provide the basis for an interdisciplinary discussion of both the theoretical and applied aspects of these surface analytical techniques. The goal is to demythologize the subject of particle bombardment and also to bridge the gap that often exists between researchers in the fields of SIMS and FABMS. Scientists with a modest knowledge of mass spectrometry should gain a clearer understanding of desorption techniques and how they can be applied.

The book is organized into three sections. The first contains the most recent views on fundamental aspects of particle bombardment. Discussions of ^{252}Cf plasma desorption and laser desorption mass spectrometry have been included for comparison. The second section addresses the issues involved in instrument design, covering work on liquid metal and FAB ion guns. The last part presents representative applications of these bombardment methods.

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The historical development of particle bombardment was presented by R. E. Honig as a retrospective lecture at the 32nd Annual Conference on Mass Spectrometry and Allied Topics in San Antonio, Texas, in 1984. This excellent lecture has subsequently been published, and I recommend it for those who wish additional background on the topic [Honig, R. E. In *The 32nd Annual Conference on Mass Spectrometry and Allied Topics— Retrospective Lectures;* Finnigan, R., Ed.; American Society for Mass Spectrometry: East Lansing, MI, 1984; Honig, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1985,** *66,* 31–54].

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Molecular Secondary Ion Mass Spectrometry

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Progress in molecular secondary ion mass spectrometry (SIMS) is presented, with emphasis on applications and the mechanism of ion formation. The mechanism involves three processes: (1) energy conversion at the surface, (2) ion/molecule and electron transfer reactions in the selvedge, and (3) unimolecular dissociations of internally excited gas phase ions. The role of matrix effects in mechanistic studies is discussed, as are experiments which use chemical reactivity to gain insights into mechanism. The use of tandem mass spectrometry (MS/MS) in ion structural determinations in SIMS and other desorption ionization experiments is illustrated. MS/MS provides evidence for unimolecular dissociations of gas phase ions, which appear to underlie much of the fragmentation seen in molecular SIMS. Cases of strong molecule-surface interactions can result in dissociation in situ, however, and examples are collected. Applications of molecular SIMS in quantitative and trace analysis, chromatography, studies of ion chemistry, catalysis, and imaging are reviewed. Developing areas in molecular SIMS include highly endothermic fragmentations and ion beam induced surface reactions.

It is a remarkable feature of secondary ion mass spectrometry (SIMS) that considerable chemical information is accessible through the procedurally simple physical technique of sputtering. SIMS--especially under low primary ion flux conditions ("static SIMS," also known as "molecular SIMS" when applied to compounds)--provides information on molecular weight and molecular structure and allows isotopic analysis. The surface sensitivity of SIMS permits its use in imaging, in monitoring of surface

reactions, and in characterizing the "local atomic structure" of
the surface of a complex material. High primary ion fluxes are
useful for depth profiling and for analysis of materials dissolved
or suspended in liquid matrices. Some characteristics of molecular
SIMS are given in Table I.

This review focuses on the phenomenon of molecular SIMS--that
is, the physical and chemical bases for its many analytical
applications. The applications themselves are also reviewed. The
coverage is somewhat historical, emphasizing progress which has
come out of this and other laboratories in the past five years.
SIMS is discussed in the context of experiments using related
desorption ionization (DI) methods, especially laser desorption
(LD) and fast atom bombardment (FAB).

It will be helpful to start by considering the status of
molecular SIMS as of 1980, with particular reference to a review
(1) which summarized progress in molecular SIMS to that date.
Perceptions of the basic mechanism in SIMS have changed
surprisingly little in the ensuing period, although considerable
advances have occurred in experimental and instrumental techniques.
In 1980 fast atom bombardment mass spectrometry using liquid
matrices did not exist, matrix effects in SIMS were little
explored, and there were few SIMS studies of catalysts. Analysis
of high molecular weight compounds by SIMS was hampered by the
limitations of the quadrupole and low mass range sector analyzers
which were used almost exclusively at that time.

While there has been rapid progress in each of these areas,
the generation of polyatomic ions is still seen in the terms
presented in 1980: (i) the conversion of energy from the form in
which it is originally applied into net translational energy of a
molecule sufficient to allow it to leave the surface, (ii) the
ion/molecule and other chemical reactions which occur at the
interface and in the selvedge and which transform the surface
molecules of interest into gas phase ions suitable for mass
analysis, and (iii) secondary processes which alter the nature of
the ion beam after it leaves the interfacial region, especially
fragmentation due to unimolecular dissociation of internally

Table I. Some characteristics of molecular SIMS

Analyzer types	Quadrupole, sector(s), time-of-flight
Vacuum requirements	10^{-10} - 10^{-6} torr
Primary ion	Ar^+, Xe^+, Cs^+, O_2^+ common
Primary ion current	$< 1 \times 10^{-8}$ A cm^{-2} for static SIMS, but higher currents sometimes acceptable
Primary ion energy	500-10000 eV common
Sample composition	Involatile organics, inorganics, and organometallics; semiconductors; adsorbed gases
Physical form of sample	Foils; bulk solids; compressed pellets; frozen and liquid matrices
Sample size	100 µg - 10 ng common; bulk (multi-layer) samples often used
Sputtering yields	1% - 0.01% common
Secondary ion energy distribution	About 3 eV average, depending on sample; no high energy tail as with atomic species
Mass range	Usually below 2000 amu; > 20000 possible
Detection limit	$\leq 10^{-15}$ g for salts
Other features	Surface-sensitive; isotope-specific; can distinguish molecular weight, molecular structure; some capability for depth profiling and imaging

excited gas phase ions. The selvedge (the term is due to Rabalais (2)) is the plasma formed at and immediately above the surface during sputtering.

Figure 1 is an early representation of these three regimes with their distinctive physical and chemical phenomena (3). In this early picture, energy interconversion was considered as a form of isomerization--"energy isomerization"--leading to an expression of the excitation in a form more or less independent of the type of energy input. Vibrational excitation, especially of the lower frequency modes corresponding to intermolecular motion, was considered as the basis for desorption. Activation of surface phonons expresses these ideas in different currency.

Three types of ionization processes were distinguished (1) as contributing to the ions observed in molecular SIMS spectra: direct desorption of precharged materials, cationization/anionization, and electron ionization (Equations 1-3, respectively). The equations illustrate overall reactions and do not attempt to explain detailed mechanistic steps.

$$C^+A^- \ (s) \longrightarrow C^+ \ (g) + A^- \ (g) \tag{1}$$

$$M^O \ (s) \longrightarrow M^O \ (g) \xrightarrow{\ C^+\ } [M+C]^+ \ (g) \tag{2}$$

$$M^O \ (s) \longrightarrow M^O \ (g) \xrightarrow{\ e^-\ } M^{+\cdot} \ (g) \tag{3}$$
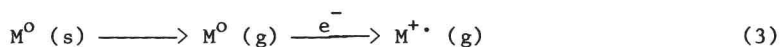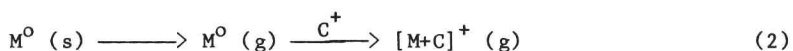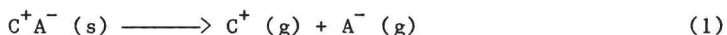
Desorption of precharged materials (i.e., salts) is a highly efficient process, since energy is not channeled into both an ionization step and a desorption step; previously existing ions are simply transferred from the solid phase to the gaseous phase. This effect may be seen in the ease with which SIMS spectra of quaternary ammonium salts are obtained (4). Derivatization of zwitterions to yield species with a net charge illustrates the same point. Cationization or anionization of neutral molecules by attachment of metal ions, protons, and other charged species is the second commonly observed ionization process in molecular SIMS (5). This may involve desorption of neutral molecules

```
                    ┌──────────────────────────────────┐ collision
                                                         induced
        unimolecular                                     dissociations
        dissociations                ┌──────────┐                ┌──────────┐   ┌──────────┐
                              - - - - │ analysis₁│ - - - - - - - │ analysis₂│---│detection │
                                      └──────────┘                └──────────┘   └──────────┘
                            extraction
```

surface | selvedge | vacuum

VIBRATIONAL DESORPTION ———————— Weak intermolecular bonds break to form $C^{o,+}$, $A^{o,-}$, and M^o

REACTION ——————————————— Simple, fast bond formation or dissociation to form, e.g., $(C+M)^+$

IONIZATION ———————————— Electron ionization to form $M^{+\cdot,-\cdot}$

TYPES OF IONS leaving the surface are approximately independent of the ionization method.

ENERGY ISOMERIZATION

Transformation to a common form

ENERGY DEPOSITION

Unique ion formation processes (FI)

TYPES OF FRAGMENTATIONS are governed by the nature of the desorbed ions as described by gas phase ion chemistry.

ION ABUNDANCES depend on internal energies which vary between and within each method.

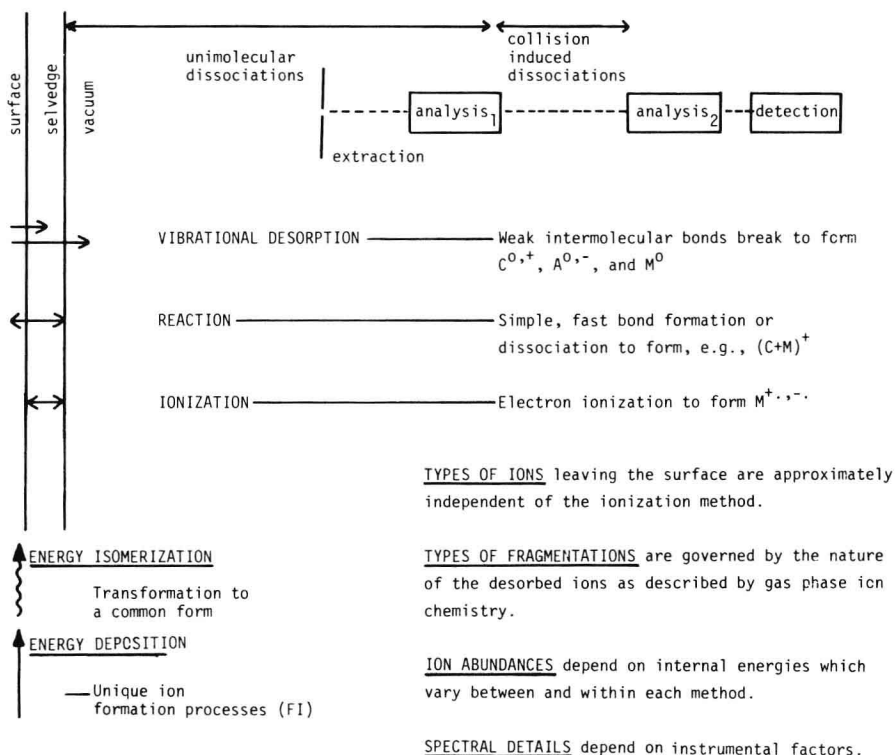SPECTRAL DETAILS depend on instrumental factors.

Figure 1. Early proposal of a unified model for SIMS and other desorption ionization experiments. Reproduced with permission from Ref. 3. Copyright 1983, Elsevier Science Publishers B.V. (First presented at a conference on ion formation from organic solids, Münster, West Germany, 1981.)

concurrently with metal ion production, followed by reaction in the selvedge to form an adduct. Electrons present in the selvedge as a result of secondary electron emission can ionize neutral molecules to give the third type of ionization process seen in molecular SIMS. This process, formation of cation and anion radicals, is not particularly efficient, but it can sometimes lead to abundant ions, for example, in SIMS spectra of polycyclic aromatic hydrocarbons (1).

In addition to those ions formed during or soon after primary ion impact, as in the processes just described, other ions arise through subsequent events. Unimolecular reactions of ions, akin to metastable decompositions in magnetic sector mass spectrometry, occur in the free vacuum. The resulting fragment ions have intensities which contradict the notion that SIMS is a "soft" ionization technique, although some fraction of the ion production events can be so characterized.

In the discussion of mechanism given below, support for the concepts just outlined will be marshalled from newer experimental results which are accomodated by the above model and which call for intact emission of molecules. It should be noted, however, that in the case of a strong molecule–substrate interaction, fragmentation probably occurs directly at the surface. Clearly this is the case when polymers are examined by bombardment techniques. Almost all molecular SIMS experiments employ static conditions in which virgin surface is selected for analysis. Typical maximum ion current densities of 1×10^{-8} A cm^{-2} correspond to ca. 6×10^{-5} ions s^{-1} per surface molecule of 10 Å^2 area. This allows sputtering times to exceed one hour before there is a significant probability of examining modified surface material. However, examples are being encountered and will be discussed below where surface chemical reactions ("beam damage") do occur under static SIMS conditions in particular cases. This can produce extensive cleavages of high energy bonds and result in distinctive SIMS fragmentation behavior.

Data will also be given for other desorption ionization experiments which support the general notion of energy

isomerization, although no detailed treatment of energy interconversion is attempted. The third aspect of the SIMS mechanism, unimolecular dissociation of isolated gas phase ions, is also the topic of some of the newer experiments reported below, including those which utilize tandem mass spectrometry to characterize these events directly.

Mechanism

The fundamental nature of the desorption process is a continuing subject of controversy. The extensive literature on sputtering of atomic species has led to models which adequately explain most aspects of atomic SIMS (6, 7). Molecular SIMS, however, presents a greater challenge, and the means by which a large biomolecule becomes an ion are less clearly understood. Models have been proposed (8,9), and some current models of molecular desorption are described in the proceedings of this symposium (10-13). Our own qualitative but not untested views are given above and more extensively in the sections which follow. A significant question on which different views have been taken is this: Is fragmentation of stable, strongly internally bonded organic molecules upon primary ion impact significant, or is this overwhelmingly the result of delayed gas phase dissociations of energetic ions? There are dynamical calculations which confirm that such instantaneous dissociations can occur (14), and there are angle-resolved SIMS data which have been interpreted as evidence that they can be a major source of fragment ions (15). Much of the data for bulk samples presented and cited herein, including the similarities in behavior observed when comparisons are made with gas phase processes, lead to the opposite conclusion. Time-resolved experiments in the picosecond range might resolve this issue but are not now accessible.

A feel for the nature of the mechanistic problem can be had by examining the environment near the surface after an impact event using simple calculations and widely-accepted assumptions. It has been noted that a primary ion current density of 1×10^{-8} A cm^{-2}

corresponds to 6×10^{-6} ions $\mathring{A}^{-2}$ s^{-1}. This means that, on the average, each area of 6×10^{6} $\mathring{A}^{2}$ receives one "hit" by a primary particle each second. Because of the very large relative distances and long times between impacts, each must be considered as an isolated event. Consider that a single impact can sputter ten particles, each of mass 200 amu and kinetic energy 2 eV. Using the relation that kinetic energy = $1/2$ mv^{2}, where m is mass and v is velocity, the velocity of a 2 eV particle of mass 200 amu is 1.39×10^{5} cm s^{-1}, or 1.39×10^{13} $\mathring{A}$ s^{-1}. The kinetic theory of gases makes possible the calculation of absolute pressure for particles of any kinetic energy through the relation $P = 1/3$ nmv^{2}, where n is the number of particles per unit volume (16). Since the mass of a 200 amu particle is 3.32×10^{-22} g, the absolute pressure for ten such particles of 2 eV energy is 1.8×10^{10} $\mathring{A}^{3}$ torr. If an appropriate volume can be justified, the pressure in this volume can be calculated by simple division. Suppose the selvedge region is a sphere of radius 50 $\mathring{A}$; half of the sphere is below the pre-impact level of the surface, and half is above it. The volume of this region is 5.2×10^{5} $\mathring{A}^{3}$. The pressure in this volume is thus 3.5×10^{4} torr as long as the ten particles remain within the sphere--a time of roughly 3.6×10^{-12} s, assuming particles originate at the center of the sphere and there are no collisions.

It should be stressed that these calculations are of the most elementary nature and are meant only to give a feel for what the actual situation may be. If the chosen conditions are varied extensively, however, the basic conclusions remain unchanged. It is interesting to note that even within a volume of 10^{10} $\mathring{A}^{3}$ the pressure will still be about 1 torr. In this case particles will have existed for around 10^{-10} s (hundreds of bond vibrations). A recent FAB study (17) found evidence for sputtering from bulk glycerol, based in part on the sputtering of a 10^{5} $\mathring{A}^{3}$ volume with each primary particle impact (corresponding to ejection of more than 1000 glycerol molecules per Xe primary atom). Very high local pressures are clearly involved in FAB, a situation which supports the assumptions made in our own comparatively conservative

calculation. The picture of the selvedge that emerges is that of a very hot, high pressure region in which multiple collisions are possible. This can explain many of the experimental observations discussed below.

Matrix effects. While theoretical approaches to mechanistic studies form a large part of the literature, it is also possible to gain insight through observations based on chemical modification of the system of interest. Modification of the sample matrix provides one chemical approach to mechanistic information. Several different types of matrix effects have been observed. For example, Figure 2 shows SIMS spectra of mixtures of a quaternary ammonium salt and ammonium chloride. The neat compound gives an abundant intact cation at m/z 390, as expected for a precharged species. Rearrangement with loss of cyclohexene to give a fragment at m/z 308 is the dominant fragmentation process observed in the SIMS spectrum of this compound. Similar fragmentations, occurring via elimination of stable neutral molecules, are also observed when quaternary ammonium ions are collisionally activated (18). If NH_4Cl is physically mixed with the organic salt at dilutions of 1:2 and then 1:20, an increase occurs in the intact cation abundance relative to the fragment abundance (19). This effect occurs without a decrease in signal-to-noise ratio, even at dilutions as high as 1:1000. At such high dilutions the ratio of m/z 390 to m/z 308 levels off at a value of about 5:1. A tentative explanation for this matrix effect is that the intact cation is initially solvated by NH_4Cl. The NH_4Cl then forms NH_3 and HCl in a desolvation process which serves to take up internal energy from the cation. This loss of internal energy results in decreased fragmentation. The desorption/desolvation sequence suggested seems reasonable in view of observations (see below) of solvent-cation adducts in FAB (20), and of self clustering in FAB spectra of NH_4Cl itself (21) and SIMS spectra of low temperature matrices. An alternative explanation is that sputtered cations are collisionally relaxed by interaction with matrix species in the selvedge, a process only subtly different from