



Mechanistic studies of the desorption ionization process in fast atom bombardment mass spectrometry  
by Jentaie Shiea

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in  
Chemistry

Montana State University

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Abstract:

The mechanisms involved in Desorption Ionization (DI) continue to be a very active area of research. The answer to the question of how involatile and very large molecules are transferred from the condensed phase to the gas phase has turned out to involve many different phenomena. The effect on Fast Atom Bombardment (FAB) mass spectra of the addition of acids to analyte bases has been quantitatively investigated. Generally, the pseudomolecular ion ( $M+H^+$ ) intensity increased with the addition of acid, however, decreases in ion intensity were also noted. For the practical use of FAB, it is important to clarify the reasons for this acid effect. By critical evaluation, a variety of different explanations were found. However, contrary to other studies, no unambiguous example was found in which the effect of "preformed ions" could adequately explain the observed results. The mechanistic implications of these findings are briefly discussed. The importance of surface activity in FAB has been pointed out by many researchers. A systematic study was conducted, involving the addition of negatively charged surfactants to samples containing small organic and inorganic cations. An enhancement of the positive ion spectra of these analytes was observed. The study of mass transport processes of two surfactants was performed by varying the analyte concentration and matrix temperature in FAB. The study of the desorption process in SIMS by varying the viscosity of the matrix solutions shows that such studies may help to bridge the mechanisms in solid and liquid SIMS and, in the process, increase our understanding of both techniques. It also shows that in the ionization process (precursor ion formation versus ion-molecule reactions), the role of radiation chemistry, transport processes, and the desorption process show characteristic changes with matrix viscosity. The ionization efficiency and competition effects in FAB for the precharged alkali and tertiary alkyl ammonium (TAM) ions were investigated. The competition between alkali ions themselves and alkali ions and TAM ion is too weak to be detected. However, TAM ion as well as the alkali ions, have a strong suppressing effect on the ion signal from amine bases. The most significant finding is a strong enhancement of  $Cs^+$  ion signal at a low matrix temperature. It was also found that the formation of mixed alkali chloride clusters in FAB are formed with a statistical distribution. Finally, a 2D molecular dynamics calculation simulating the bulk desorption in FAB was performed. The shockwave, spinodal decomposition, extensive cooling and the molecular desorption are all observed from the simulation. These are in agreement with the concepts presented earlier in the "phase explosion model".

MECHANISTIC STUDIES OF THE DESORPTION IONIZATION PROCESS  
IN FAST ATOM BOMBARDMENT MASS SPECTROMETRY

by

Jentaie Shiea

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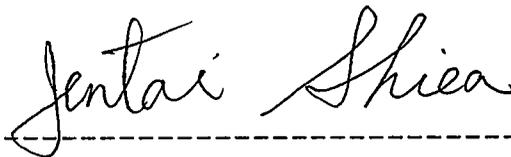
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## ABSTRACT

The mechanisms involved in Desorption Ionization (DI) continue to be a very active area of research. The answer to the question of how involatile and very large molecules are transferred from the condensed phase to the gas phase has turned out to involve many different phenomena. The effect on Fast Atom Bombardment (FAB) mass spectra of the addition of acids to analyte bases has been quantitatively investigated. Generally, the pseudomolecular ion ( $M+H^+$ ) intensity increased with the addition of acid, however, decreases in ion intensity were also noted. For the practical use of FAB, it is important to clarify the reasons for this acid effect. By critical evaluation, a variety of different explanations were found. However, contrary to other studies, no unambiguous example was found in which the effect of "preformed ions" could adequately explain the observed results. The mechanistic implications of these findings are briefly discussed. The importance of surface activity in FAB has been pointed out by many researchers. A systematic study was conducted, involving the addition of negatively charged surfactants to samples containing small organic and inorganic cations. An enhancement of the positive ion spectra of these analytes was observed. The study of mass transport processes of two surfactants was performed by varying the analyte concentration and matrix temperature in FAB. The study of the desorption process in SIMS by varying the viscosity of the matrix solutions shows that such studies may help to bridge the mechanisms in solid and liquid SIMS and, in the process, increase our understanding of both techniques. It also shows that in the ionization process (precursor ion formation versus ion-molecule reactions), the role of radiation chemistry, transport processes, and the desorption process show characteristic changes with matrix viscosity. The ionization efficiency and competition effects in FAB for the precharged alkali and tertiary alkyl ammonium (TAM) ions were investigated. The competition between alkali ions themselves and alkali ions and TAM ion is too weak to be detected. However, TAM ion as well as the alkali ions, have a strong suppressing effect on the ion signal from amine bases. The most significant finding is a strong enhancement of  $Cs^+$  ion signal at a low matrix temperature. It was also found that the formation of mixed alkali chloride clusters in FAB are formed with a statistical distribution. Finally, a 2D molecular dynamics calculation simulating the bulk desorption in FAB was performed. The shockwave, spinodal decomposition, extensive cooling and the molecular desorption are all observed from the simulation. These are in agreement with the concepts presented earlier in the "phase explosion model".

## INTRODUCTION

It was a substantial development in Analytical Chemistry when the mass spectrometer (MS) was first successfully used in determining the structure and molecular weight of chemicals in this century. Until recently, sample volatility was one of the principal requirements for mass spectrometry. Samples are amenable to electron impact ionization (EI) only if the sample molecules interact with energetic electrons (usually 70 eV) in the gas phase (see Figure 1). Traditional sample-inlet systems, at best, transport the sample only to the periphery of the ion source. By virtue of its vapor pressure, the molecules have to diffuse into the central region of the ionization chamber (focal point) to be ionized. The ions are extracted from the chamber by a small repulsion voltage (ca. 50 V) applied to the ion source and later focused and accelerated by a series of ion optical lenses. The requirement of adequate sample volatility imposed a practical limit of roughly 1,000 a.m.u. or less on the molecular weight of samples that were amenable to EI or chemical ionization (CI) mass spectrometry.

The development of desorption-ionization (DI) techniques has broken the shackles of sample volatility in mass spectrometry (Watson, 1985). This breakthrough has been especially important in the biochemical area, where most compounds (e.g. peptides, proteins and nucleic acids) are

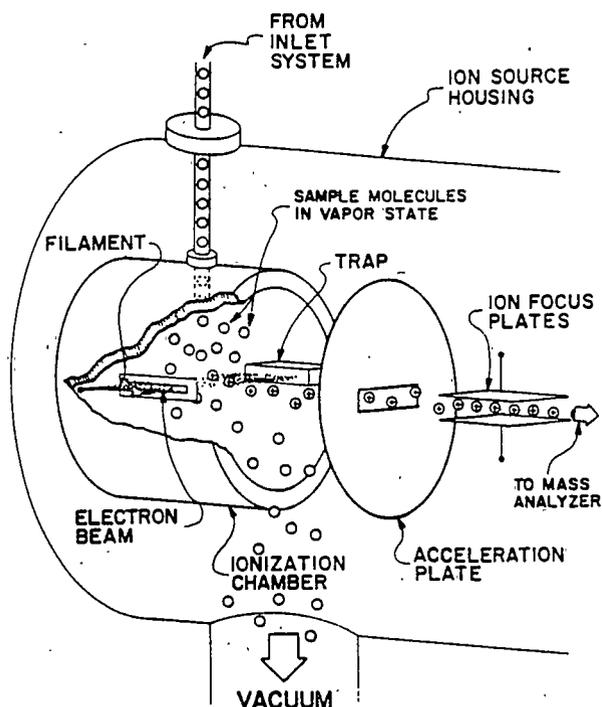


Figure 1. Diagram of EI ion source in mass spectrometer (from Watson, 1985).

quite polar or are in the form of polymers having very high molecular weights and thus low or no appreciable vapor pressure. In addition, these compounds are with few exceptions thermally labile and decompose easily at the operational temperature in EI.

There are four main DI techniques. These are particle induced DI techniques which include Secondary Ion Mass Spectrometry (SIMS), Fast Atom Bombardment (FAB), and Plasma Desorption (PD) and laser induced DI technique- Laser

Desorption (LD). In particle induced DI technique, the analyte is introduced into the ion source in the condensed phase (pure solid or as a solution in a viscous solvent). Desorption and ionization are induced by bombardment by energetic particles. The techniques are distinguished by the type of particle used for bombardment. For example, in SIMS a solid surface is bombarded by ions; in FAB by atoms; and in PD by fission fragments. In LD, the energy is deposited in the sample by pulse from the laser beam. A schematic representation of the four techniques is presented in Figure 2. It is interesting to note that although the energy of the primary ions (or atoms) of the various techniques range over several orders of magnitude, the resulting mass spectra are similar. That is, most of the ions formed contain the intact molecule in the form of an adduct with  $H^+$ ,  $Na^+$ ,  $K^+$ , or other cations or clusters. One rarely observes a peak for the molecular ion per se. Fragmentation is generally less than that observed in EI. Because of this particular characteristic, DI is termed a "soft ionization method".

A short summary of the history of developments in DI techniques will be given here. In 1969 Beckey published a mass spectrum of glucose, a polar compound of very low volatility (Beckey, 1969). The method he used, so called Field Desorption (FD), proved to be the precursor of the family of desorption ionization methods. In FD, ions are desorbed by the combined action of heat and the very high

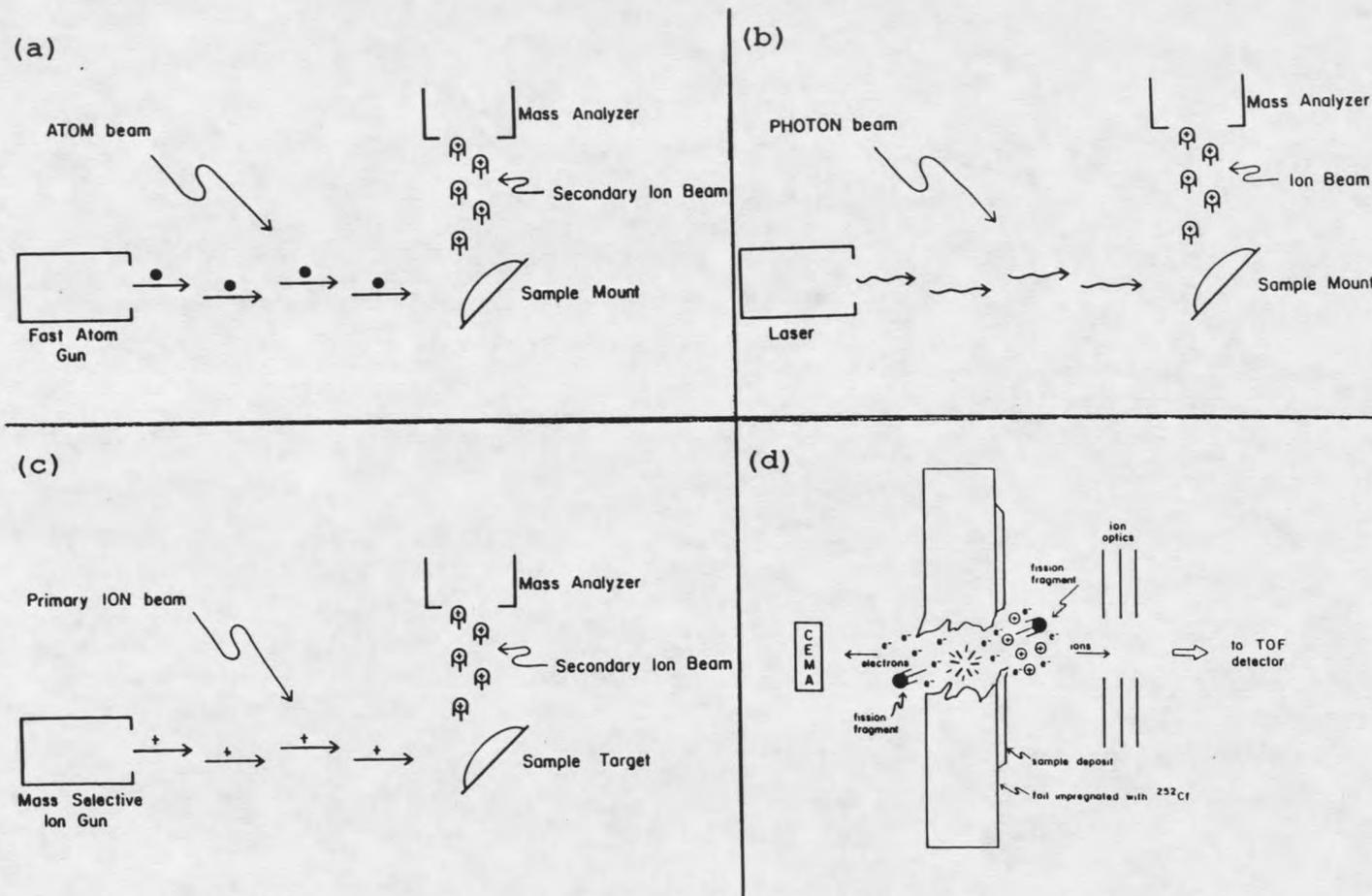


Figure 2. Schematic representation of the four variations of desorption ionization (DI) techniques- (a) FAB, (b) LD, (c) SIMS, (d) Cf PDMS (from Watson, 1985).

fields present in the source (Beckey, 1977). Beckey's work was built on an understanding of the physics of field emission and ionization. His contribution was the translation of this knowledge into a device having practical value in the molecular sciences.

The development of particle induced DI techniques began with the introduction of californium-252 Plasma Desorption Mass Spectrometry (PDMS) in 1974 by MacFarlane and coworkers (Torgerson et al., 1974). In this method, heavy ions (with hundreds of MeV of kinetic energy from the spontaneous fission of  $^{252}\text{Cf}$ ) bombard a solid matrix and induce desorption and ionization processes. Large polar thermally labile molecules are able to survive intact and to sublime from the surface as ionized species (Torgerson et al., 1974; MacFarlane and Torgerson, 1976; MacFarlane, 1982; McNeal and MacFarlane, 1981; Hakansson et al., 1982). After the initial report, it was soon realized that an essential feature of PDMS was that the deposition of energy is highly concentrated and that the excitation is very short-lived. This technique has been very important for the analysis of biological compounds.

In 1976, Benninghoven demonstrated that the mass spectra of amino acids derived from keV ions impinging on the surface of a thin film of the sample are essentially the same as those observed in  $^{252}\text{Cf}$  PDMS (Benninghoven, 1976). This method, Secondary Ion Mass Spectrometry (SIMS), had been used routinely in surface analysis of inorganic species or organic

compounds but had never been applied to thermally labile biomolecules. So far, two types of SIMS have been developed. Atomic SIMS is used in surface analysis of inorganic materials under dynamic conditions. In this technique, high primary ion dose densities (usually  $>10^{-6}$  A·cm<sup>-2</sup>) at ultra-low pressure (ca.  $10^{-10}$  torr) was used. Low ion fluxes ( $<1 \cdot 10^{-8}$  A·cm<sup>-2</sup>) and low pressure ( $< 10^{-5}$  Torr) are used in molecular SIMS to effect depth profile measurement. Most of the organic compounds were analyzed by molecular SIMS under static conditions.

In 1978, Posthumus et al. showed that excitation by short ( $< 10$  ns) laser pulses created mass spectra that are essentially the same as in <sup>252</sup>Cf PDMS and SIMS (Posthumus et al., 1978). This third variant of DI technique is called Laser Desorption (LD).

The fourth variation, introduced by Barber et al. in 1981, uses a keV beam of neutral atoms for bombardment and is called Fast Atom Bombardment (FAB) (Barber et al., 1981a; 1981b). However, it was later shown that the use of atoms as opposed to ions was of little importance. Instead, what is significantly different about FAB is the medium from which desorption-ionization occurs; a liquid solution matrix. Since the development of this technique in 1981, several thousand papers dealing with FAB have been published. Today, FAB is used in routine analysis in most major mass spectrometry laboratories.

Since FAB has become such an important DI method in

analytical mass spectrometry and because the majority of this dissertation deals with the desorption process in FAB (see below), a detailed description of this technique will be given here.

### Fast Atom Bombardment Mass Spectrometry

FAB is the most recent DI technique and has acquired the widest usage in the fields of analytical bioorganic and pharmaceutical chemistry. This is because of

- 1) quick and easy sample preparation
- 2) a relatively stable and persistent ion signal
- 3) high flexibility for the FAB source to add-on several types of mass spectrometers.

In FAB, the analyte is usually dissolved in a polar, viscous, low boiling point solvent such as glycerol, diethanolamine, ethylene glycol, and thioglycerol. The sample is then mounted on a probe that is introduced through a vacuum-lock assembly such that the sample surface rests at the focal point of the instrument.

The beam of fast atoms is produced by first ionizing the corresponding gas to produce ions and accelerating the ions (in the range of 6 to 10 keV) into a dilute gas where the fast ions capture an electron, thereby being converted from fast ions to fast atoms (Lew, 1976; Frank, 1983; Mahoney et al., 1983; Rudat and McEwen, 1983). FAB with xenon atoms gives the best spectra among those gases that have been studied (Morris

et al., 1983; Martin et al., 1982). The beam of bombarding atoms is usually maintained at a large angle relative to the axis of the beam of ions extracted by the ion optics. A typical incidence angle is between  $45^\circ$  and  $70^\circ$  (Martin et al., 1982). Many particles (ions and neutrals) are disrupted from the surface and are spewed over a wide solid angle. Positive or negative ions focused by the ion optics provide a glimpse of the process in the form of a mass spectrum. The ions available are by no means solely related to the analyte, even if pure. Many ions emanate from the glycerol or solvent itself. A diagram of the arrangement of the atom gun and sample probe in the mass spectrometer is illustrated in Figure 3(a).

The FAB technique has been successfully used in analyzing numerous biological and organic compounds (such as peptides, pigments, saccharides, polar lipids, nucleic acids and underivatized, polar, high-molecular-weight, nonvolatile organic synthetic compounds), however, the FAB mass spectrum does not always provide a simple straightforward indication of the molecular weight. Evidence for the intact molecule comes in the form of adduct ions consisting of the molecule together with a  $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{H}^+$ . Dehydrated adduct ions frequently produce intense peaks also. A peak representing the molecular ion is rarely observed, as one might find in EI. Figure 3(b) is a typical FAB mass spectrum of a dipeptide (tyrosyl-arginine) in glycerol. The spectrum shows a peak for the

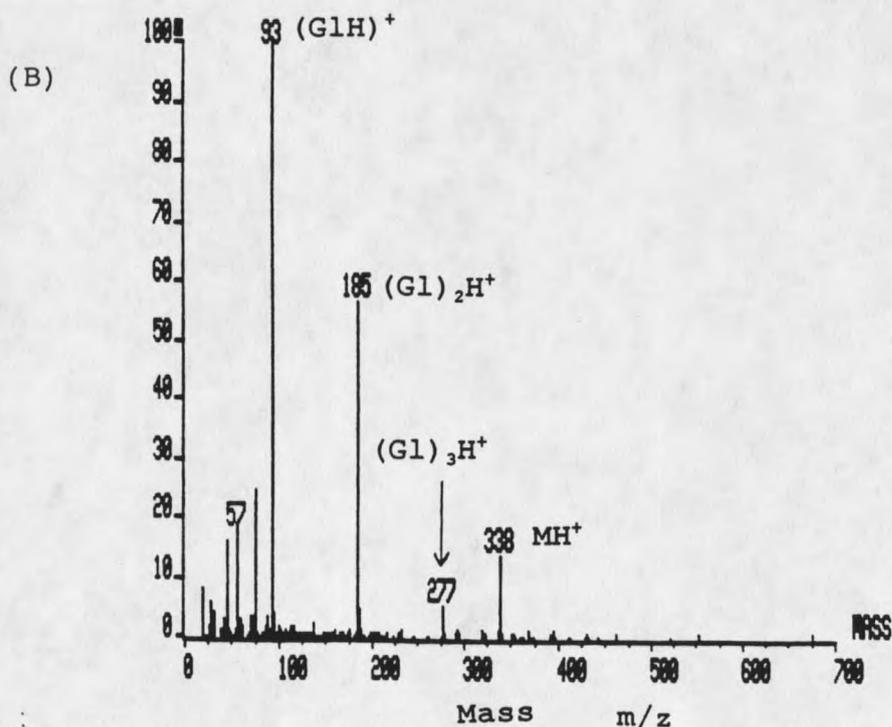
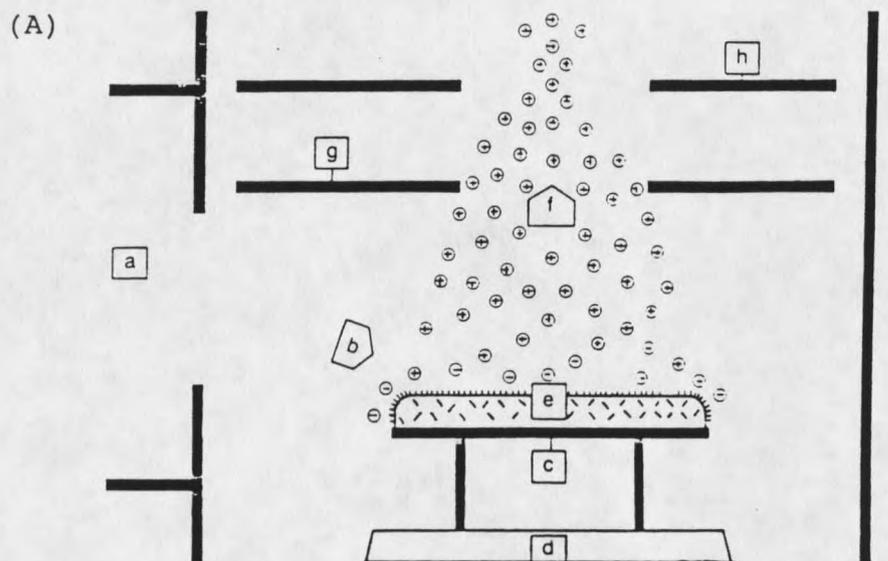


Figure 3. (A) Schematic diagram of the FAB source. (a) atom gun; (b) atom beam; (c) metal sample holder; (d) end of probe; (e) sample in low volatility solvent; (f) positive ion beam; (g) ion extraction plate; (h) lens system leading to the mass analyzer (revised from Barber et al., 1982). (B) FAB mass spectrum of 0.1 mol% dipeptide (tyrosyl-arginine) in glycerol.

adduct ion  $(M+H)^+$  (also named pseudomolecular ion) at  $m/z$  338. The ions at  $m/z$  136 are fragments from the dipeptide. All of the other major ions arise from the glycerol matrix (major glycerol fragments:  $m/z$  29, 31, 45, 57, 75; glycerol monomer:  $m/z$  93; glycerol dimer:  $m/z$  185; and glycerol trimer:  $m/z$  277). The chemical noise, the low intensity background of ions occurring at every mass, which is characteristic in FAB mass spectra is also observed in this spectrum. As can be seen in Figure 3(b), the most useful information obtained from most FAB spectra is the molecular weight of the analyte. Usually limited information about the structure is obtained from a few ion fragments in the mass spectrum (only one fragment from the dipeptide is observed in the mass spectrum).

Recently, a number of studies using FAB/MS/MS have succeeded in deriving structural information from small molecules (e.g. peptides). In this technique, the intact protonated molecular ion produced in the ion source is selected by a first mass analyzer and then accelerated into a field free collision chamber. Many ions can be made to dissociate as a result of collisions with the neutral molecules (e.g. air or argon) preexisted in this region. The fragment ions generated by this process are analyzed by the second mass analyzer located after the collision chamber. Although this technique has been successfully used in analyzing small and simple molecules, large and complex compounds usually give very complicated fragment mass spectra

and it becomes very difficult to interpret the spectra.

FAB has been successfully used in qualitative analysis of many biological compounds. However, it is known for its lack of accuracy in quantitative analysis. It has been observed that in FAB mass spectra, the signal intensity from the analyte usually is not proportional to its concentration in the solution. The situation becomes worse when the sample contains more than one analyte. In many cases, it has been shown that with two analytes at equal-concentration, one analyte often dominates in the mass spectrum whereas the signal from the other analyte may show only weak intensity or totally disappear. Some analyte ions cannot compete with the ions formed by the matrix itself and are not seen in the FAB spectra. These suppression effects have restricted the development of FAB for quantitative analysis.

The research community has spent a great deal of energy in trying to solve practical problems encountered in FAB. From these studies, four major factors have been suggested as playing the main roles in determining good FAB spectra:

- 1) bringing the sample to the solution
- 2) bringing the sample to the surface layers
- 3) precharging the sample before the bombardment
- 4) choosing the right matrix

Later, each of these factors will be shortly discussed. There are also various theoretical studies on the fundamental mechanisms of the desorption ionization process in FAB.

Several of these studies and models derived from them will also be presented and discussed shortly in this section.

#### Bringing the Sample to the Solution

There is general agreement that secondary ion currents are stronger if the analyte molecule is actually dissolved, either in the matrix liquid or in a cosolvent, as opposed to being present as a suspension. It is thus an important task for the FAB practitioner to find a way to bring the analyte into solution in the matrix. Cosolvents such as water, methanol, chloroform and dimethyl sulfoxide have been used, miscible with the less volatile matrix solvents.

#### Bringing the Sample to the Surface

In many cases, ion currents are observed to increase when the analyte is enriched at the surface of the matrix. Experimental measurements are easily made on surface tension, and thus surface-active analytes have been most readily studied. Several approaches have been conducted to concentrate the sample in the upper layer of the matrix (Zhang et al., 1984; Ligon and Dorn; 1986a; Ligon and Dorn; 1986b) and have led to improvements in analyte-to-matrix signal ratio. For example, derivatization may increase the surface activity of the molecule, or one may add a surfactant with an opposite charge to bring the molecule to the surface through charge neutrality in the surface layers.

### Precharging the Sample Before the Bombardment

The observation that the majority of the ions detected in FAB are pseudomolecular ions (i.e.  $(M+H)^+$ ) suggests that they are formed before the bombardment. Most FAB practitioners have added some salts or acids to the sample try to increase the ratio of the precharged analyte molecules in the matrix. In some cases, the addition of acids or salts does increase the  $(M+H)^+$  signal, however, in other cases the method fails. The overall effect of adding acids and salts to the sample is still unclear, however, the practice of using this strategy to enhance the precharged molecules still is very common and acceptable in routine FAB analysis.

### Choosing the Right Matrix

Although all parameters used in controlling the primary beam and ion optics of the mass spectrometer are critical to obtain good FAB spectra, many of these parameters are not variable or even optimized on commercial instruments. However, it is easy to change the liquid matrix. Indeed, the choice of matrix in FAB can spell the difference between success and failure. The multiple contributions of the matrix have been discussed (dePauw, 1986; Fenselau, 1984; Todd, 1986, Todd and Groenewold, 1986). It has been suggested that the matrix should be chosen with the objectives of optimizing and persisting absolute secondary ion currents. Its selection can

also influence fragmentation and signal-to-noise ratios. According to the studies, several characteristics of the matrix such as viscosity, vapor pressure, and background contribution (i.e. chemical noise level) have been suggested as important factors in determining a good FAB mass spectrum (Falic, et al., 1986; Ligon, 1983a; Todd, 1986; Wong et al., 1986; Katz et al., 1986; Gower, 1985). From these studies, a general picture of a good FAB matrix in qualitative analysis can be given as follows:

- 1) the matrix itself should possess low volatility and enough fluidity to prolong the ion currents and the viscosity should not be too high to inhibit the self cleaning process (i.e. the radiation products formed by FAB are removed by the desorption process itself).
- 2) the matrix should be able to dissolve the sample well (i.e. bring the analyte molecule into the solvent) and also provide a precharged analyte molecule.
- 3) Compared to the matrix, the surface activity of a given analyte should be high.
- 4) A matrix is preferred which provides a clear window (i.e. low chemical noise level) in the mass range of analytical interest.

Only very few existing organic solvents match all the criteria described above (Cook et al., 1989). It needs to be mentioned here that the matrix selection is also highly dependent on the chemical properties of analyte itself. These criteria are the

reasons why, in many cases, the FAB practitioner must try several matrices to get a signal from an analyte. However, for some compounds, regardless of the choice of matrix, the desired analytical signal may still be totally missing. This was not understood until some of the researchers began to investigate the mechanisms of the FAB process.

Understanding the mechanisms of desorption-ionization is important not only from a theoretical point of view but also from the perspective of increasing the analytical utility of the method. To discuss the molecular SIMS and FAB mechanisms, atomic SIMS represents a useful starting point, since it provides a vocabulary and a theoretical foundation on which to build (Pachuta and Cooks, 1985). Three major mechanistic studies of atomic SIMS which address different aspects of atomic desorption will be outlined. The discussion will be followed by the models suggested for FAB and molecular and liquid SIMS.

#### Collision Cascade Model

The model involves momentum-transfer processes (Thompson, 1968; Sigmund, 1969; Sigmund, 1981). The primary atom enters a surface and gradually slows down as it strikes surface and substantial atoms until it has lost its excess kinetic energy. The collisions displace target atoms, as well as alter the initially linear trajectory of the primary ion. Recoiling target atoms can strike other atoms, and this so-called

"collision cascade" proceeds until the impact energy is dissipated in a volume radiating outward from the point of impact. In the course of the cascade, some atoms may acquire momentum in a direction toward the surface and, if the energy of such an atom is greater than the surface-binding energy, the atom will be emitted from the surface. In this case, the kinetic energy of the ejected atoms is usually high. The model was formulated by Sigmund and has received wide currency, primarily because it provides a quantitative basis for many observations. However, it is still the subject of intense debate and its restriction to binary collisions is thought by some to be an oversimplification (Cooks and pachuta, 1987).

#### Thermal Spike Model

This model explains the emission of low-energy and high-energy particles from the DI process and it is very useful in molecular SIMS (Kelly, 1977; Sigmund and Claussen, 1981). Kelly and Sigmund considered that bombardment of a material induces elastic collisions between atoms in the matrix, and this collision-induced excited region (the "slevedge") behaves much like a dense gas at high temperature. Emission of low kinetic energy particles occurs by evaporation from the "slevedge". Atoms with high-energy can be emitted by a direct recoil process which is similar to the processes suggested in the collision cascade model (Magee, 1983; Schultz et al.,

1983; Rabalais and Chen, 1986). This involves ejection of high-energy-recoil particles produced by direct momentum transfer from primary ions. The thermal spike model explains the emission of low and high energy particles, but cannot explain the emission of the vast majority of particles with intermediate energies.

#### Bond Breaking Model

This model is often invoked to explain ion emission from ionic compounds (Soldzian, 1975; Gnaser, 1984). A typical lattice (e.g. NaCl) will contain a valence band of anionic states and a conduction band of cationic states, separated by a band gap (e.g. 10 eV for NaCl) (Williams, 1979; Poole et al., 1975). According to this model, half of the lattice energy is consumed when a cation is removed, but in order to remove a neutral an electron has to cross the band gap and the atom must go to the gas phase, which is energetically less favorable. Then, for ionic compounds the emission of ions is preferred, when the lattice energy is much less than the band gap. The model can also be used to explain ion emission from covalent compounds. As long as there is some polar character, a band gap will exist, and ion emission will be favored if the lattice energy is much less than this band gap. While the bond-breaking model is appealing, it applies mainly to polar materials, and it fails to explain the enhanced emission of negative ions from oxygenated surfaces.

In addition to the main models, several other models have also been suggested. Some of them tried to improve the existing models and can only be applied to specific cases. These models include a "molecular model" (Thomas, 1977), "band structure model" (Van der Weg and Bierman, 1969; Kelly and Kerkdijk, 1974; Murray and Rabalais, 1981), "local thermal equilibrium model" (Andersen and Hinthorne, 1973), "surface polarization model" (Williams and Evans, 1978), "local bond-breaking model" (Yu and Mann, 1986), "sudden perturbation model" (Krueger, 1983), and "electron-tunneling model" (Yu and Lang, 1983; Yu and Lang, 1986). Unfortunately, none of the above models can explain all the experimental results.

Molecular species were observed as contaminants in SIMS spectra. However, molecular SIMS did not evolve until after the development of the static SIMS method. As described before, the key innovation in static SIMS was the use of a low primary ion current density to minimize sample damage which is opposite to that in molecular SIMS. In the mechanism of molecular emission in SIMS, a first step might be to attempt to correlate molecular data with the wealth of atomic SIMS theory. There may be similarities between the processes resulting in atom and in molecule emission, but an energetic collision cascade alone would seem an improbable means by which to eject intact molecules, particularly large biomolecules. Most of the molecular SIMS models that have been advanced therefore incorporate a thermal component into

the mechanism. In the following discussion, several different views of molecular desorption will be described, beginning with the models most closely resembling those in atomic SIMS and then toward models focused mainly on FAB or molecular and liquid SIMS.

#### Classical Dynamics Simulations of Collision Cascade

A number of the computer simulations of desorption process in SIMS have been developed by Garrison and co-workers (Garrison and Winograd, 1982; Brenner and Garrison, 1986; Garrison, 1982; Garrison, 1983; Garrison, 1985). The simulations are based in large part on those first developed by Harrison (Harrison et al., 1968; Harrison et al., 1973; Harrison and Delaplain, 1976). It was found that some aspects of molecular SIMS can be explained by assuming a collision cascade model which is developed from atomic SIMS. In a typical calculation, parameters such as primary ion mass, energy, and angle, and the size, depth, and crystal structure of the target are first defined. Classical equations of motion are then applied to compute the position and momentum of each particle as a function of time (Harrison et al., 1978). The time scale is in femtoseconds, with molecular ejection usually occurring in less than 200 fs. Classical dynamics simulations have a number of obvious advantages and disadvantages. The major advantage is that it allows semiquantitative predictions of actual behavior, including the

species ejected and their energy and angular distributions. It is conceptually simple and has a basis in reasonably well-understood atomic sputtering theory. The disadvantage is that it is primarily a model for sputtering, and not for ionization; parallels must therefore be established between neutral and ion emission.

#### Preformed Ion Formation Model

The idea that precharged analyte ions are observed preferentially to ionized forms of the initially neutral analyte is the key to the preformed ion or precursor model (Day et al., 1980; Benninghoven, 1983a and b). Benninghoven, drawing chiefly from results for monolayers of amino acids on clean metal surfaces, describes this idea for pseudomolecular ion emission. In this model, Benninghoven suggested that an excited region (10-100 Å in diameter) is formed around the path of the bombarding particle, due to the dissipation of its kinetic energy. Very rapid energy transfer causes emission of the precursor ions from the surface, with the high probability of maintaining their charge state during the whole process. Fragmentation occurs in some cases and may result from transfer of a large amount of energy near the impact point or from gas-phase decomposition of an excited molecule.

#### Gas Flow Model

The essential part of this model is that gas may be

formed in the cavity (created by primary atom impact) as a result of the thermal spike effect. This gas may then flow from the cavity into vacuum and various chemical reactions may also occur during this process (Michl, 1983; David et al., 1986; Urbassek and Michl, 1987). The model was suggested by Michl et al. as follows: at very short times after primary ion impact ( $< 10^{-12}$  s) collision cascades result in secondary ion formation, but at somewhat longer times ( $> 10^{-12}$  s) thermal processes take on a dominant role. Ions arising from collision cascades are called "first batch" ions, while those emitted from thermal spikes are called "second batch" ions. A thermal regime is presumably created during quenching of the collision cascade as energy is transferred to the cold surroundings in the solid. As the thermal spike spreads, second batch particles are ejected in an "explosive expansion of high-pressure gas into vacuum". During this expansion, clusters can be formed by recombination, and molecular fragmentation can occur. Ionization is thought to originate in the spike also.

#### Vibrational Desorption Model

The model was developed by Cooks and co-workers (Unger and Cooks, 1981; Busch and Cooks, 1982; Cooks and Bush, 1983; Busch et al., 1983b; Zakett et al., 1981). On the basis of the observation that the mass spectra obtained by SIMS, FAB, LD, and PD are essentially the same, these authors suggested

that although the initial form of energy deposition is different among these techniques at some point, the energy should be present in a common form. This so-called "energy isomerization" has been proposed to involve energy transfer to low-energy vibrational and translational models. This causes heating and emission of electrons, photons, neutral molecules and ions. As in the gas flow model, the concepts of quasi-thermal emission and "selvedge" reactions (e.g. ion-molecular reaction) are thought important by Busch et al. (1983). The model also includes the idea that for organic samples examined under static conditions most fragmentation results from unimolecular decay of metastable ions in the free vacuum.

#### Droplet or Spray Model

The idea of this model originates from the high sputtering yields and the ejection of vibrationally cold cluster ions and pseudomolecular ions in FAB (Vestal, 1983; Wong and Rollgen, 1986). The model suggests the following sputtering mechanism: First, the incident particle penetrates into the liquid, probably with a mean penetration depth between 50 and 100 Å, and creates a collision cascade which contains dense gas. A high gas pressure is built up causing the ejection of large clusters of matrix and sample molecules originally from the dense cascade region. Later, the decomposition of these clusters produces the pseudomolecular ions. The unimolecular decay of the clusters also gives rise

to some vibrational cooling of the remaining molecules. Sputtering of radiation damage products also takes place. As for the ionization process, it is assumed that the clusters initially formed are randomly charged, and their rapid decomposition leads to the most stable ions. Therefore, the ion intensity distribution reflects the ion chemistry in solution.

#### Gas Collision Model

The model primarily deals with the sequential chemical reactions occurring in the gas phase in the collision cascade. It was suggested that the incident primary atom forms ionized fragments from matrix or analyte molecules in the collision cascade, and that these react to give protonated molecules and clusters through a sequence of proton transfer and clustering reaction in a dense gas type condition (Sunner et al., 1988a). The intensity of the intact molecules is then dependent on the gas-phase basicity not the liquid-phase basicity. A kinetic analysis by the authors showed that significant number of gas-phase collisions may occur. This also strongly indicates that some thermalization must take place. From the model a "residence time distribution" in the  $10^{-10}$  to  $10^{-9}$  second range for the ions in the "gas" was deduced. The best agreement with experiments was found for a distribution that was inversely proportional to time. This is also the expected distribution if ion-ion recombination is the dominant ion loss



























































































































































































































































































































































