

Surface Characterization with Ion-induced Desorption and Multiphoton Resonance Ionization

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It is known that high-molecular-weight, thermally labile molecules can be desorbed intact using keV ion beams. This knowledge has led to numerous applications of fast atom bombardment and secondary ion mass spectrometry (SIMS) by mass spectrometric detection of the desorbed ions. Here we show that these measurements can be enhanced significantly by using resonance-enhanced laser ionization to softly ionize the neutral component of the desorbed flux. This experimental configuration can produce sensitivity improvements of several orders of magnitude over SIMS while adding a certain degree of selectivity to the ionization process itself. Examples of this performance will be presented using a wide variety of molecules, including polycyclic aromatic hydrocarbons, organic polymers, molecular salts and biologically important molecules. Results from model systems to complex samples are discussed, along with their implications for submicron molecular imaging using this technique.

INTRODUCTION

It has been 24 years since Benninghoven introduced to us the concept of static SIMS.¹ From this initial idea we have, of course, expanded our vision of ion/solid interactions manifold. The journey through organic SIMS, liquid matrix SIMS, time-of-flight SIMS and angle-resolved SIMS has indeed been a fascinating one. The work emanating from Benninghoven's laboratory has exerted a central influence upon those of us working in the field and has helped to establish the SIMS methodology as a core surface characterization technique.

Can static SIMS measurements be improved? It is a difficult challenge because primary ion doses are necessarily $< 10^{13}$ ions cm^{-2} , suggesting that the methodology must work exceedingly well right from the start. Obviously, however, improvements have been steady and rapid over the last 22 years. In fact, it is the implementations of new instrumental tools that have allowed this field to retain its vigor through such an extended period.

Possibly the most difficult issue to deal with in static SIMS experiments involves matrix ionization effects. The ion yield of molecular species, in particular, can vary over many orders of magnitude. These yields are also strongly dependent upon the surface electronic properties. Moreover, it is not possible to enhance molecular ion yields by O_2^+ or Cs^+ bombardment as is traditionally done by dynamic SIMS users. This approach is clearly in violation of the basic principles of static SIMS. Cationization or anionization rarely mitigates these problems.

Since 1982,² our group has focused on the use of laser techniques to post-ionize neutral species that desorb from the surface. Not only can resonance-enhanced laser ionization frequently improve sensitivity by several

orders of magnitude by efficiently sampling the more abundant neutral flux, but it can also produce soft and selective ionization.

Initially, our experiments concentrated on the study of atomic photoionization using multiphoton resonance schemes.² In this experiment a pulsed laser beam is directed over the sample after a pulsed ion beam has struck the surface. In general, these pulsed laser beams operate at a fairly low repetition rate of perhaps 100 Hz or less. If the incident ion beam has a peak current density of $300 \mu\text{A cm}^{-2}$ and the pulse length is $\sim 5 \mu\text{s}$ at a repetition rate of 30 Hz, then the average current density is only 45nA cm^{-2} . A spectrum is typically averaged over ~ 1000 laser shots so the total dose will be 2.8×10^{11} ions cm^{-2} which is well within the static limit. The neutral species desorbed by these primary ions are then ionized with the laser beam. Multiphoton resonance ionization (MPRI) uses a two (or more)-step ionization process consisting of resonance excitation(s) followed by ionization. It is the resonant excitations that make MPRI unique. A resonant excitation consists of absorption of a photon that is energetically matched to a bound-bound transition in the analyte's electronic structure. As every species has its own unique electronic structure, selective excitation can frequently be performed. The primary advantages of laser post-ionization is that the efficiency of creating ions from the neutral flux is very high, near 100% for atoms, and that the ionization step is decoupled from the desorption step. This aspect of the technique offers the possibility of minimizing matrix ionization effects.

Atomic systems provide the most dramatic examples of MPRI. This results from the extreme selectivity and the impressive ionization efficiencies that are attainable in these systems. Recently, a 9 ppt detection limit for indium in silicon, along with a linear dependence of the signal on concentration, was reported.³ Other groups have also developed many innovative and interesting atomic analyses, such as: ultratrace analyses of biological samples relevant to the study of diabetes, hematology, toxicology, neonatology and neurology;⁴ a very

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elegant application of krypton-81 dating of the cosmic ray exposure of meteorites,⁵ and a novel application to genome sequencing at high speeds.⁶

The situation becomes more complex when using lasers for molecular photoionization. While many impressive results have been obtained for atomic systems, it is not obvious that molecular systems would be amenable to ion beam desorption with MPRI. The reasons for this are the possibility of fragmentation during desorption or photoionization, the potential for a reduced useful fraction (the number of countable particles) owing to the population of many rovibrational states during desorption and the degradation of ionization selectivity that results from the greatly increased number of available intermediate states that rotation and vibration provide. In fact, this selectivity reduction may be an asset because it eliminates or reduces the potential useful fraction losses that the increased number of populated rovibrational states might otherwise cause. However, it also means that all of the molecules containing the chromophore being probed by the laser will be ionized with some efficiency.

In this paper, we review the current status of molecular postionization experiments as a complementary tool to static SIMS for surface analysis. These experiments are potentially important because they may improve SIMS detection limits by several orders of magnitude in some cases. Moreover, the signals should be less prone to matrix ionization effects, opening the analyses to systems with a complex environment. Examples for a variety of systems will be presented. Finally, we speculate about the possibility that this measurement may allow submicron spatial resolution for molecules, which is a particularly challenging measurement owing to the high sensitivity that is required.

EXPERIMENTAL

A schematic diagram of our experimental set-up is shown in Fig. 1. The experiment starts with a pulse of primary ions striking the sample. It should be noted that, in pulsed experiments, the primary ion current that leaks through when the pulse is off is an important source of noise in the form of a constant secondary ion background. The pulse of primary ions desorbs ions

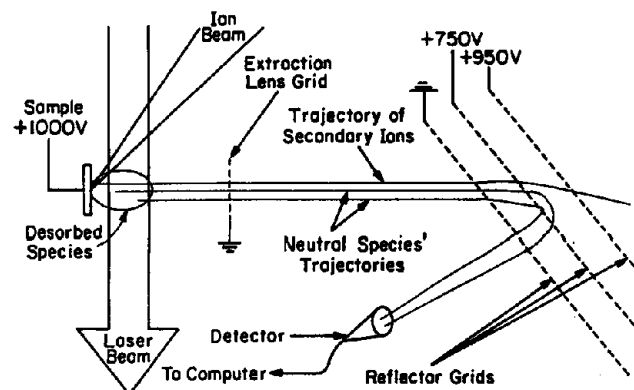


Figure 1. Schematic representation of the ion-induced desorption-MPRI-reflecting ToF mass spectrometry experiment. (See text for discussion.)

and neutrals from the surface. After a suitable delay, the laser beam is fired over the sample to ionize the ejected neutrals. Although other lasers, such as excimer lasers, may be useful for some experiments, we use an Nd-YAG-based laser system. The main advantage of Nd-YAG lasers is the ability to produce high peak powers in the Q-switched mode that, coupled with a dye laser and frequency doubling/mixing crystals, can be manipulated to obtain high-power, tunable light suitable for ionizing all elements except helium and neon. The Nd-YAG fundamental wavelengths (1064, 532, 355 and 266 nm) are also useful by themselves or for producing 118 nm light.⁷

Higher laser powers allow the irradiation of larger volumes at a given power density and MPRI is very efficient at low power densities owing to its large cross-sections. As the collection efficiencies for the neutrals depend upon the amount of overlap between the laser beam and the desorbed plume, the ability to use a larger diameter laser beam increases sensitivity. As a result, MPRI is much more sensitive than other laser photoionization schemes that require focusing of the laser beam, such as non-resonant multiphoton and single photon ionization.⁷ These approaches are also non-selective in their sampling of the desorbed species.

After MPRI of the sputtered neutrals, the photoions are extracted into the mass spectrometer for mass-selective detection. For trace analyses, where sensitivity is critical, we use a reflecting time-of-flight (ToF) system.⁸ Time-of-flight analyzers require a pulsed ion source and therefore they are well matched to pulsed Nd-YAG-based ionization. In the SIMS mode the primary ion pulse determines the ToF start time, so narrow ion pulses must be used to maintain mass resolution. However, in the MPRI mode the laser pulse determines this start time, so that much longer primary ion pulses may be used without degrading resolution. Longer pulses provide larger signals up until the point where the laser can no longer overlap the desorbed plume effectively. This contributes to the sensitivity advantage that MPRI has when using ToF mass spectrometers. More importantly, ToF systems have high transmissions (up to ~70%) and are capable of detecting all masses from every laser shot. Quadrupole and magnetic sector systems must be scanned to register each mass sequentially, thereby discarding most of the available ions. This has severe consequences for sensitivity and the ability to perform static measurements. Other benefits of ToF-based systems are their simplicity to build and operate, their low cost, and their unlimited mass range. Typically, mass range is limited by conversion efficiencies at the detector, but with sufficient acceleration of the ions, mass ranges of >100 000 amu are obtainable.⁹

An advantage exclusive to reflecting ToF systems is the first-order energy focusing that the reflecting process achieves. Time-of-flight mass resolution is severely degraded in experiments such as ours, which produce ions with broad kinetic energy distributions. This broad energy distribution is the result of the large laser beam size relative to the extraction field; i.e. the species ionized on one side of the laser beam experience a different fraction of the extraction field from those ionized on the other. The reflection process, however, compensates for this energy distribution by causing ions of dif-

ferent kinetic energies to travel different distances to the detector, thus preserving mass resolution. As if this advantage were not enough, it also helps to reduce SIMS contributions (noise) to MPRI signals by allowing the secondary ions, which experience the full extraction field, to pass through the electrostatic mirror without being reflected (if the mirror potentials are properly adjusted). Therefore, implementation of an electrostatic mirror design enhances resolution and sensitivity compared to a traditional ToF mass spectrometer!

For this system, the optimum atomic detection efficiency is $\sim 3\%$. The factors that contribute to this efficiency are: the useful fraction, which is frequently 99% or more; the spacial overlap between the sputtered plume and the laser beam, which is $\sim 25\%$ when using a $5 \mu\text{s}$ primary ion pulse; the achievable ionization efficiency, which is 100% for many atomic analytes; the instrument's transmission, which has been determined to be 13%, and the detector's conversion efficiency, which is limited to 85% by the MCP's active area.¹⁰ There are, however, many instances where this optimum detection efficiency is not realized. For many elements there are low-lying excited states that are significantly populated during desorption so that ionization saturation is not possible without focusing the laser beam so that the useful fraction and the ionization efficiency or laser spacial overlap are reduced. In addition, molecules have much lower ionization efficiencies, estimated to be limited to $\sim 1\%$ before significant photofragmentation results.¹¹ However, even with these limitations MPRI usually produces significantly better sensitivities than SIMS because the ion fraction is usually $< 10^{-2}$.

The sensitivity advantages of post-ionization techniques can be increased with the implementation of strategies for discriminating against interfering species and noise. There are, of course, many methods for discriminating against secondary ions in post-ionization techniques. An effective approach is to change the extraction field after the ion pulse has been switched off but before the laser is fired.³ In this way, the kinetic energy difference between the secondary ions and the photoions can be exaggerated. Other components may also have pulsed potentials to gate the desired signal (i.e. the electrostatic mirror of the detector). A reversal of the extraction field in-between the ion and laser pulses will inhibit the secondary ions from leaving the surface altogether. Noise can also result from ions scattering off the grids used for defining electrostatic fields in the instrument. While it is possible to make a gridless reflecting ToF system, the applicability of such a system must be examined on a case-by-case basis because mass resolution is sacrificed and a gridless system focuses the ion beams it reflects. The value of these schemes is presently being evaluated by many groups.

A critical issue in the experiment involves sublimation of the sample. This evaporation can be a considerable hindrance to obtaining reliable data. We have found that cooling the sample to $\sim 140 \text{ K}$ reduces this problem by suppressing the rate of sublimation. Not only will cooling conserve a sample that would otherwise disappear, but it may make samples that are normally vacuum incompatible, such as biological tissues, amenable to analysis. Cooling can also reduce the noise that results from a local high pressure, due to evapo-

ration, above the sample. One manifestation of this type of noise is a signal originating from the gas phase. In our experiments with molecules, we frequently see such signals if the sample cooling is inadequate. Such signals do not correlate with the primary ion current and may not reflect the surface composition, therefore they must be corrected for in order to perform an accurate surface analysis. A local high pressure above the surface can also create extraneous signals by becoming ionized through interactions with the incoming primary ions or the outgoing secondary ions. In severe cases of sublimation, the MPRI signal may go down when the ion beam is turned on, because the ion beam passes through the volume irradiated by the laser. While transversing the ionization volume, it may scatter more molecules out of this volume than it adds through sputtering. It should be noted that these effects are generally undetectable by SIMS. As a result, when performing molecular SIMS experiments, extra caution is required to avoid any inaccuracies that will result from sample alterations due to sublimation or from ions formed away from the sample.

RESULTS AND DISCUSSION

First we examine a set of polycyclic aromatic hydrocarbons (PAHs) including pyrene, carbazole, benzo[*a*]pyrene, dibenz[*a, c*]anthracene, triphenylene and coronene.¹² These molecules have rigid structures, which are not easily fragmented. An example of ion-desorbed pyrene with laser post-ionization is shown in Fig. 2. The pyrene signal at 202 amu, following absorption of 280 nm photons for both the excitation and ionization steps, is shown as a function of laser power.¹² At low laser power, a squared dependence is observed because excitation and ionization efficiencies vary with laser power. Once the excitation step is saturated, the power dependence is linear because at higher powers only the ionization rate is enhanced by increased power densities. At still higher powers, the signal levels off and will eventually fall due to photofragmentation.

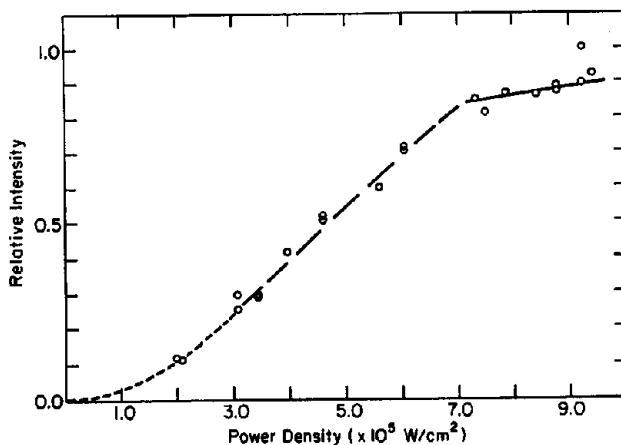


Figure 2. Response of the pyrene molecular ion intensity to 280 nm laser power density. The dashed and solid curves display the transition of the ionization signal from a two-photon dependence (----) to a one-photon dependence (—) followed by the onset of losses to fragmentation (—).

Photofragmentation during the ionization step has the potential to limit sensitivity and to make qualitative determinations more difficult. While the other post-ionization schemes have been characterized as 'hard' or 'soft', MPRI has the capability to be either. Simply by turning the laser power up or down, the absorption of photons in excess of those required for ionization can be encouraged or discouraged. This tunable fragmentation using benzo[*a*]pyrene and 280 nm light is shown in Fig. 3.¹² The excess energy from absorption of extra photons can cause fragmentation of the ion via the ladder switching mechanism.¹³ Not all molecules yield strong molecular ion peaks at low laser power. In some systems, fragmentation can occur from the excited neutral prior to ionization.¹⁴ Even when fragmentation cannot be avoided, it frequently is not a serious limitation because the base peak in the spectrum is still usually a structurally specific fragment suitable for performing most measurements.

In our initial PAH study, subfemtomole detection limits were demonstrated for these robust molecules.¹² These detection limits are at least two orders of magnitude better than for SIMS analyses because PAHs have inherently small ion fractions. When the SIMS and MPRI signals for carbazole and pyrene are compared (after correcting for the differences in the primary ion currents used for each measurement and the laser spacial overlap factors), the SIMS signal intensities are found to be ~1% and ~2% of the MPRI intensities, respectively.¹⁵

Such low ion fractions are not limited to neutral molecules such as PAHs. This is evidenced by sodium's ion fraction when desorbed from a sodium chloride crystal.

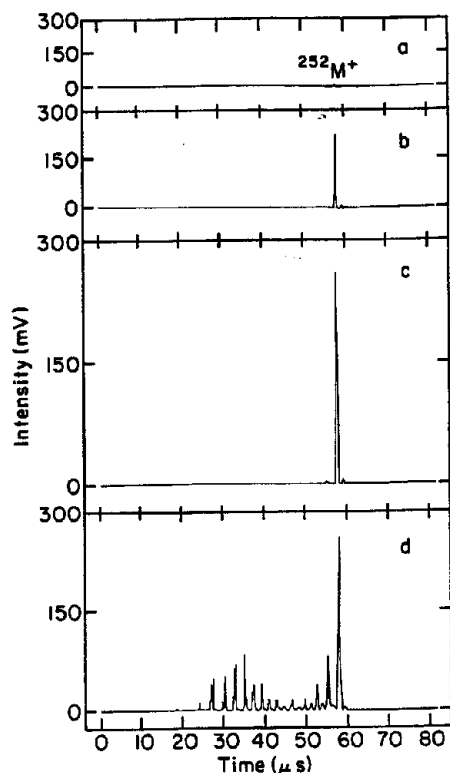


Figure 3. Time-of-flight MPRI mass spectra of benzo[*a*]pyrene ion-desorbed from a silicon surface at various 280 nm laser intensities: (a) 1.9×10^4 W cm⁻²; (b) 1.2×10^5 W cm⁻²; (c) 3.0×10^5 W cm⁻²; (d) 2.0×10^6 W cm⁻².

This value is 3×10^{-4} from a freshly cleaved <100> surface.¹⁶ In addition, many ionic molecules have been shown to have similar behavior owing to a number of neutralization mechanisms, including the loss of a small ionic fragment, which may be operating during desorption.¹⁷ An example of this is shown in Fig. 4, which shows the SIMS and MPRI spectra of phenyltrimethylammonium chloride.

In order to demonstrate that this technique can be applied successfully to a variety of materials, a number of polymers have been examined.¹⁸ In these studies, the monomers and other fragments observed contain an aromatic chromophore suitable for 280 nm ionization. In the case of polystyrene, a thick film on a gold substrate yields peaks of <250 amu. When a thin film (1×10^{-7} g cm⁻²) is prepared on a gold substrate, fragment peaks are observed up to ~1000 amu, corresponding to up to nine monomer units with or without losses of one or more carbons and hydrogens. The high mass region of this spectrum is shown in Fig. 5. The reason for this fragmentation distribution dependence on film thickness probably arises from the large amount of polymer chain entanglement in thick films. This would retard desorption without fragmentation. Thin films are less entangled so that desorption of larger fragments may occur. These results reflect trends observed with other desorption-based techniques.^{19,20} If we were to examine even thinner films we may even be able to observe the oligomer distribution of the polymer sample, as has been observed with SIMS. However, detecting such high masses requires significant post-acceleration (up to 20 kV) for adequate detector response, and when using SIMS, special preparation procedures must be used (i.e. silver substrate) to ensure adequate ion yields through cationization. Consequently, MPRI may prove useful for examining polymers in complex samples that do not have sufficient ion yields to perform a SIMS measurement.

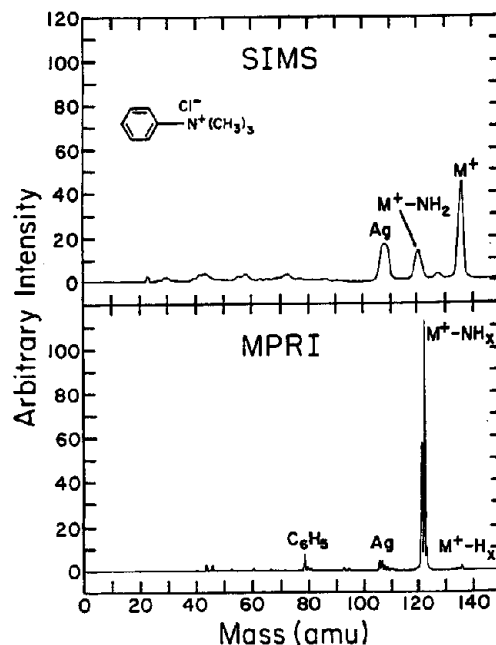


Figure 4. Time-of-flight SIMS and MPRI (280 nm, 0.260 W) mass spectra of a submonolayer of phenyltrimethylammonium chloride desorbed from a silver substrate.

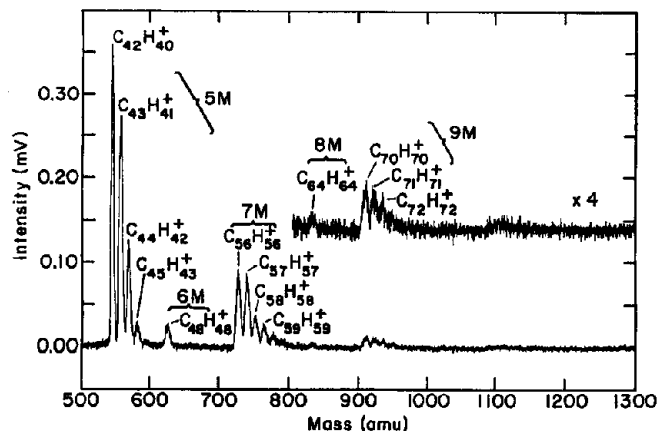


Figure 5. High mass region of MPRI mass spectrum of a thin film of polystyrene on a gold substrate. MPRI was accomplished using 280 nm light at a power density of $6.9 \times 10^5 \text{ W cm}^{-2}$. The numbers refer to the number of monomer (M) units in the chain.

Biomolecules are another important class of molecules that have been examined.²¹ Detecting biomolecules opens up a great number of potential applications for MPRI of ion-desorbed neutrals. It also demonstrates that molecules more fragile than PAHs can be examined with this technique. Of the biomolecules that we have studied (tryptamine, typtophan, serotonin, phenylalanine, adenine and β -estradiol), two are amino acids and the other four are either precursors to or biologically active compounds. All six biomolecules contain (in addition to an aromatic ring) non-aromatic rings, alkyl side-chains and/or functional groups that might be susceptible to cleavage from the parent molecule. In all cases, a strong signal from the parent ion or a structurally significant fragment ion is obtained. Even though the base peak in the serotonin spectrum is a fragment, a very good sensitivity for serotonin is demonstrated. In fact, a detection limit of 40 fmol of serotonin on a silicon surface has been achieved. Also observed is the linear dependence of this signal upon concentration, as shown in Fig. 6.

Will it be possible to apply what we have learned about well-characterized systems to those involving complex mixtures? To test this we have examined National Institute of Standards and Technology's stan-

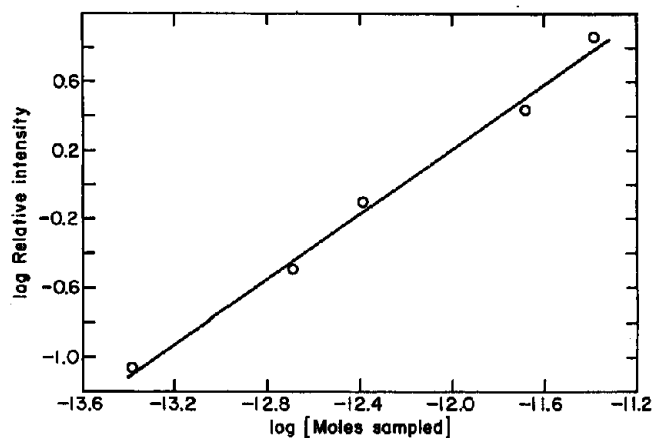


Figure 6. The MPRI intensity of the serotonin 146 amu base peak vs. the concentration of serotonin in the ion beam sampling area. See Fig. 5 and the text for experimental details.

dard reference material 1650, which consists of diesel exhaust particulates. These PAH-containing particles can cause carcinogenesis if they are inhaled. An understanding of their production and surface compositions may, therefore, aid in developing cost-effective processes and pollution control devices that specifically reduce the particles that pose the greatest risk. This analysis determined that the particles' total PAH coverage is $\sim 74\%$, and that only PAHs with two or three rings are present in significant amounts.²² This last point is important because these smaller PAHs are not considered to be very carcinogenic.

Finally, the high sensitivity of MPRI detection may open up the possibility of submicron molecular imaging. Previously, no technique has had the requisite sensitivity for chemically identifying molecules desorbed from such very small areas. This potential is being pursued in our laboratories with a liquid metal ion gun (LMIG)-based ToF-SIMS system that has an MPRI capability. Using an LMIG it is possible to probe an area of $< 400 \text{ nm}^2$.²³ The difficulty in such a measurement is that there are $\sim 10,000$ atoms or 1600 molecules in a 400 nm^2 area. One particularly exciting application of this technology would be the imaging of single biological cells.

As a first step towards realizing this goal, we have recently demonstrated the ability to apply ion-induced desorption MPRI to the detection of molecules in frozen water matrices, which are used to simulate biological tissues.²⁴ The MPRI and ToF-SIMS spectra of frozen $1.07 \times 10^{-3} \text{ M}$ tryptophan in water solution are shown in Fig. 7. These spectra look virtually identical to the spectrum for a submonolayer of tryptophan on a silicon substrate. Note the significant advantage in sensitivity with MPRI. The detection limit determined for this system corresponds to 3.6×10^5 molecules in the surface region sampled by the ion beam. If these molecules were packed together on the surface, they

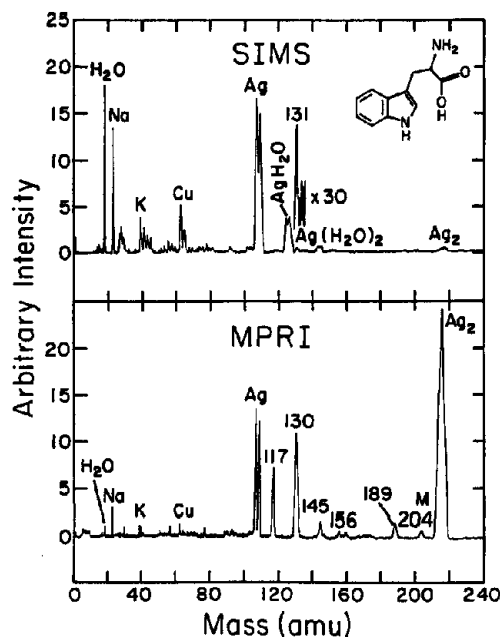


Figure 7. Time-of-flight SIMS and MPRI (280 nm, 0.285 W) mass spectra of frozen $1.07 \times 10^{-3} \text{ M}$ tryptophan in water solution on a silver backing.

would cover an area of 900 nm². Submicron molecular imaging certainly appears feasible, especially as there are a multitude of possibilities for improving upon these results.

However, it is likely that sensitivity will be limited by different factors in a high primary ion current/count rate experiment, such as the one that produced the results presented here, and a low current/count rate experiment, like imaging analysis. The high current experiment is currently limited by the background secondary ion counts. Recently, another, rather sophisticated, way to discriminate against these ions without pulsing the extraction field has been described. This new secondary ion discrimination method²⁵ utilizes an extraction lens that produces a steady-state inversion of the extraction field above the target. By passing the laser on the other side of the field inversion than the sample, photoions are effectively extracted while secondary ions are continuously rejected. It will be interesting to see how these new developments affect the ultimate capabilities of these techniques.

PROSPECTS AND CONCLUSIONS

We believe that ion beam-induced desorption coupled with MPRI is an exciting new methodology for analyzing molecules on surfaces. The excellent sensitivities and the moderate molecular selectivities attainable with this technique will allow it to make important contributions to many areas of science.

While the molecular results outlined in this paper are quite promising, it is clear that there are many opportunities for improved sensitivities through the use

of: better sample preparation procedures; optimized laser schemes (no attempt was made to optimize the schemes used here); improved mass spectrometers (we now have a second-generation instrument whose mass spectrometer has significantly better transmission (~50%) and better mass resolution (~10 000 compared to ~100)); new, more powerful lasers (which can be used to increase the spacial overlap and/or ionization efficiencies and is used with the new instrument); and shorter primary ion pulses (which increase the spacial overlap efficiencies). While these improvements imply a potential sensitivity increase of about three orders of magnitude, it is unclear if this is a realistic expectation in light of the differences between these two experiments.

There are also ways to improve the sensitivity and selectivity of the photoionization step. Sensitivity could be improved by limiting photofragmentation. One approach to this is to use picosecond or femtosecond lasers, which produce very high peak powers. This would presumably avoid fragmentation because there is not enough time for it to occur before the molecule is ionized. Another approach is to access a different excited state that is not disposed to fragmentation, if there is one. More elaborate ionization schemes, which access more intermediate levels or autoionizing states, may also increase the selectivity of the ionization.

Acknowledgements

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