

# Evidence for the formation of dynamically created pre-formed ions at the interface of isotopically enriched thin films

Jordan O. Lerach and Nicholas Winograd\*

**A novel approach to elucidate the ionization mechanism for the  $[M + H]^+$  molecular ion of organic molecules is investigated by molecular depth profiling of isotopically enriched thin films. Using a model bi-layer film of phenylalanine (PHE) and PHE-D<sub>8</sub>, the results show formation of an  $[M + D]^+$  molecular ion for the non-enriched PHE molecule attributed to rearrangements of chemical damage due to successive primary ion impacts. The  $[M + D]^+$  ion is observed at the interface for 19.9 nm in the enriched-on-top system and 9.9 nm for the enriched-on-bottom system. This ion formation is direct evidence for dynamically created pre-formed ions as a result of chemical damage rearrangement induced by previous primary ion bombardment events. Copyright © 2012 John Wiley & Sons, Ltd.**

**Keywords:** SIMS; isotope; interface; deuterium; fundamentals; depth profile

## Introduction

Due to advances in three-dimensional chemical imaging using secondary ion mass spectrometry (SIMS), it is important to understand the fundamental ionization processes involved in layer-by-layer removal during molecular depth profiling. Various groups have reported different methods to investigate the interfaces of two dissimilar materials. For example, water-ice overlayers on the surface of a sample have been employed to improve ionization.<sup>[1]</sup> Irganox delta layers have been utilized to achieve control of film thickness and roughness, and in some cases, the films possess the same sputter yield, leading to fewer artifacts.<sup>[2]</sup> However, ionization efficiency is still not under control when different molecules are involved. Here, a new method is sought to generate an interface between two thin films as chemically similar as possible, yet mass spectrometrically differentiable.

Deuterium-labeled molecules have proven fruitful in the isolation of the identity of the proton or deuterium donor responsible for ionization. In one case, a complex system of fatty acids in a matrix of varying water or D<sub>2</sub>O concentrations was used to elucidate the proton transfer mechanism.<sup>[3]</sup> However, if the system is as simple as a pure film of one analyte, the identity of the proton donor is difficult to determine. It is possible, however, to prepare a two-layer film of a non-enriched molecule and an enriched analog. Molecular depth profiling of this two-film system, with the focus being the interface, should provide unequivocal evidence for the origin of the proton responsible for ionization.

In this study, we utilize an enriched form of phenylalanine (PHE) to provide large amounts of deuterium which would become available upon fragmentation of the molecule following primary ion impact. PHE-D<sub>8</sub> (Fig. 1b) was chosen due to its high level of enrichment at very stable C-D sites. The amino and carboxyl groups remain protonated since these sites may be able to exchange protons with neighbors. Thus, the possibility of exchange not due to primary ion impact is negligible. Molecular depth profiling is performed, and exchange of a deuteron from fragmented

PHE-D<sub>8</sub> molecules is observed in the form of the  $[M_{\text{PHE}} + D]^+$  molecule, yielding strong evidence for dynamically created pre-formed ions (DCPI).<sup>[4–6]</sup>

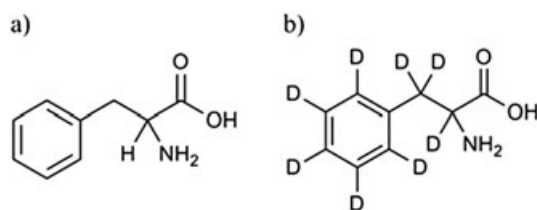
## Materials and methods

PHE-D<sub>8</sub> was purchased from CDN Isotopes (Pointe-Claire, Quebec, Canada), and PHE was obtained commercially from Acros Organics (Geer, Belgium). Both samples were used without further purification. Bi-layer samples were created in a previously described, laboratory-built physical vapor deposition chamber<sup>[7]</sup> attached to a time-of-flight ToF-SIMS system described previously.<sup>[8]</sup> Each layer was 100 to 300 nm in thickness as determined by a quartz crystal microbalance (QCM). Briefly, an alumina crucible containing 0.2 g of either analyte was brought to sublimation temperature by resistive heating of a tungsten filament. The resulting sublimate is diffused for uniformity by a grid above the crucible, then adsorbed onto a clean Si shard. The shard is attached to a Cu block *via* double-sided copper tape (3M, Saint Paul, MN) which is in contact with a liquid N<sub>2</sub> cooled QCM, from which thickness was monitored. The deposition chamber, which is also connected to the SIMS instrument, was able to hold two crucibles enabling a multi-layer film with two components to be created and analyzed without having to expose the sample to atmosphere.

The sample stage was cooled to 90 K to minimize damage accumulation during erosion. Also, at such temperatures, molecular motion is not expected between the two analytes in the bi-layer system. Mass spectra were collected at 3 KHz with a 100 ns pulsed primary ion beam of 20 keV C<sub>60</sub><sup>+</sup> ions with intermittent erosion

\* Correspondence to: Nicholas Winograd, The Pennsylvania State University, Chemistry, University Park, Pennsylvania, USA. E-mail: nxw@psu.edu

Penn State University, Chemistry, University Park, Pennsylvania, USA



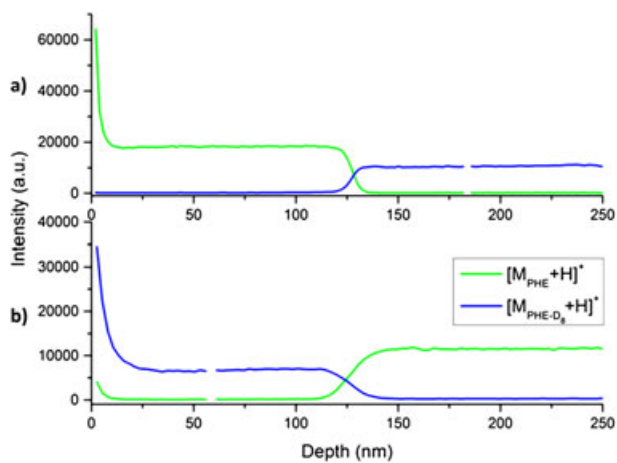
**Figure 1.** Structures of the phenylalanine and phenylalanine- $D_8$  molecule.

cycles of 7 s. A primary ion beam of between 100 and 140 pA was rastered across an area of  $240 \times 300 \mu\text{m}^2$  as measured by AFM profilometry. Profilometry measurements were taken on a KLA Tencor Nanopics 2100 (Milpitas, CA) in contact mode providing the researchers with accurate depth information of the sputtered film.<sup>[9]</sup>

## Results and discussion

Complementary depth profile analyses were performed on two separate bi-layer samples, where the enriched layer was either on top or bottom relative to the non-enriched layer. The respective depth profiles through each type of film are shown in Fig. 2. In each depth profile, a small increase in Molecular Ion (MI) intensity is observed followed by a rapid fall of the signal into the steady state. At the interface of each film, the MI signal for the top layer approaches zero whereas the lower layer's MI rapidly increases and reaches its steady-state value. An obvious difference can be observed between the steady-state values for the respective MI's as the PHE- $D_8$  MI has lower intensity when compared to the PHE MI. This difference is due to the lower abundance of protons within the enriched sample. This observation directly suggests that diminishing proton sources by replacement with deuterons suppresses the formation of  $[M + H]^+$  and enhances the formation of  $[M + D]^+$ .

The focus of this study is at the interface of these bi-layer systems. Consider the system with the PHE- $D_8$  film on top of the PHE film. As the depth profile proceeds, a layer of chemical damage is built up and subsequently removed as the steady state is achieved. In this region, damage is accumulated and removed at the same rate, giving a static identity to the fragments which remain near the surface of freshly exposed film. Since the identity



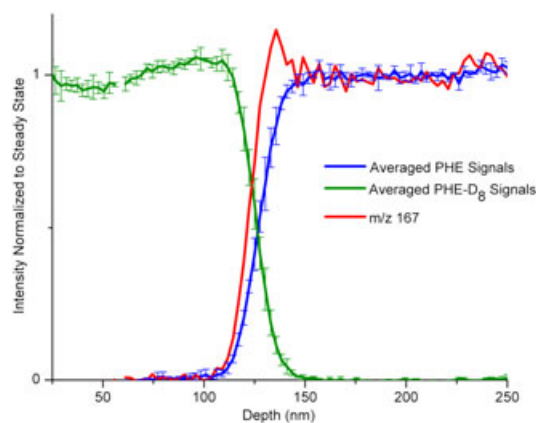
**Figure 2.** Depth profiles monitoring the  $[M + H]^+$  ions for each layer are shown for the a) enriched-on-top sample and b) enriched-on-bottom sample.

of the top film is PHE- $D_8$ , many of the fragments are deuterium rich. These fragments are subject to beam-induced mixing from primary ion bombardment, which may allow them to interact with the lower levels of the film. As this PHE- $D_8$  damage layer is brought closer to the PHE layer, perturbation of the two films occurs as fragments from the PHE- $D_8$  layer migrate into the PHE film. This mixing allows deuterium-rich damage to associate to PHE, specifically in the form of  $D^+$  ions. By monitoring the  $[M_{\text{PHE}} + D]^+$ , the source of D can be determined.

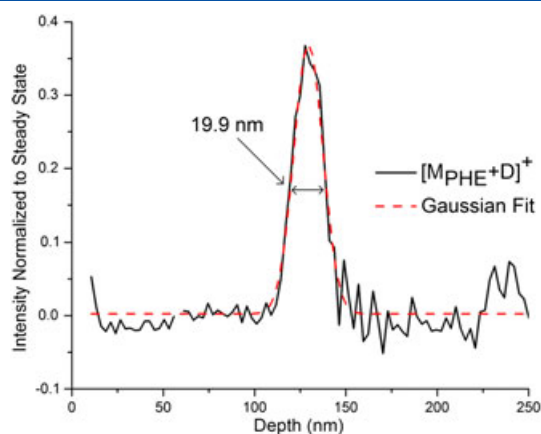
Figure 3 shows the anomalous ion signal at  $m/z$  167 relative to the common trends of ions from respective layers of the film. This plot was created after normalizing the steady-state values of common ions of each layer to unity and determining the mean and standard deviation of those values using OriginPro 8.1 (OriginLab, Northampton, MA). Ions chosen for the enriched sample were at  $m/z$  81, 98, 128, 173, 174 and 175 while analogous ions for the non-enriched sample had  $m/z$  ratios of 77, 91, 120, 128, 165 and 166. The signal at  $m/z$  167 was plotted separately given its disparate behavior resultant from the formation of  $[M_{\text{PHE}} + D]^+$  at the interface. Beyond the interface, the supply of  $[M_{\text{PHE}} + D]^+$  decays, and the remaining signal is due to the steady-state value of the  $[^{13}\text{C} M_{\text{PHE}} + H]^+$  isobar.

In order to extract the signal for  $[M_{\text{PHE}} + D]^+$  from the isobar, a sigmoidal trend was fitted to the average value of the non-enriched ions using OriginPro 8.1 and subtracted from the normalized  $m/z$  167 signal. Since the data points are normalized to the same y-value, the representative subtraction spectrum will yield information pertinent to the x-axis. Therefore, the subsequent subtraction spectrum yields a peak which represents the abundance of the  $[M_{\text{PHE}} + D]^+$  ion as a function of depth as evident in Fig. 4. After fitting a Gaussian peak to the subtraction spectrum, it was determined that the FWHM is 19.9 nm.

For comparison, a separate experiment was performed by depth profiling through a bi-layer film where the non-enriched sample resided on top of the enriched sample. The same data treatment method was used to examine these separate systems. Considering again the signal due to only  $[M_{\text{PHE}} + D]^+$  for each system at the interface, it can be seen that the width of the peak for the enriched-on-top depth profile is significantly larger than the enriched-on-bottom depth profile at 19.9 nm and 9.9 nm,



**Figure 3.** Signal due to  $m/z$  167 and average values for common ions from the enriched and non-enriched films are shown. Steady-state values have been normalized to unity. Analogous ions were chosen between the two respective samples with the exception of the ion at  $m/z$  167, due to its anomalous behavior. The peak at  $m/z$  167 is due to the abundance of the  $[M_{\text{PHE}} + D]^+$  ion. Isobaric interference at the steady-state signal is due to the  $[^{13}\text{C} M_{\text{PHE}} + H]^+$  isobar.



**Figure 4.** Signal for the the  $[M_{\text{PHE}} + \text{D}]^+$  ion is obtained by subtracting the sigmoidal line fitted to the characteristic ion trend of the PHE ions from the  $m/z$  167 signal. The FWHM of the Gaussian profile shows a finite width of 19.9 nm observed for the enriched-on-top sample.

respectively. The differences in peak widths describe what mechanisms are causing DCPI formation in each system.

In order for  $[M_{\text{PHE}} + \text{D}]^+$  to form, a species with a loosely bound  $\text{D}^+$  must reside near a PHE molecule. Considering the case with the enriched sample on top, chemical damage due to the primary ion impact will have yielded a surplus of D-rich fragments. These fragments are known to occur below the surface and, in the case of H or D, have been known to migrate within the sample. This allows D-rich fragments from the enriched layer to come into contact with PHE molecules in lower layers. This is a process in support of DCPI proposed recently.<sup>[4]</sup> Alternatively, in the case where the enriched film is on the bottom, the width of the  $[M_{\text{PHE}} + \text{D}]^+$  peak is half the size as in the preceding case. This narrowing is due to the low probability of intact PHE molecules being forced to lower depths within the sample and coming in contact with fragments from the PHE- $\text{D}_8$  molecules. It is known that the layers of a film below the surface do receive some chemical damage due to primary ion impact, however, the forces at the lower levels are greatly diminished compared to those nearer the surface, leading to less damage. The lower mobility of an intact PHE molecule relative to fragmented molecules or free deuterons limits mobility within the sample, hence the smaller width of the  $[M_{\text{PHE}} + \text{D}]^+$  signal.

The formation of DCPI is evident from the formation of the  $[M_{\text{PHE}} + \text{D}]^+$  ions. The identity of the ionizing atom is easily traced to the PHE- $\text{D}_8$  layer. Conclusions made about the  $[M + \text{D}]^+$  ion formation can analogously be stated for  $[M + \text{H}]^+$  formation due to the similarity in chemical identity. In the two cases outlined in this study, primary ion impact is responsible for the formation of D-rich fragments and mobility of the fragments within the top few layers of the film. If a D-donating species comes into near enough contact with a PHE molecule, the basic  $\text{R-NH}_2$  site may

abstract that molecule to form a DCPI. Upon successive primary ion impact, the DCPI is liberated from the confines of the film and enters into the vacuum of the ToF-SIMS instrument where it is subsequently analyzed. This has been shown to occur in the case of  $[M_{\text{PHE}} + \text{D}]^+$  and should analogously occur for the formation of  $[M + \text{H}]^+$  ions for both enriched and non-enriched samples due to the chemical similarity between H and D.

## Conclusions

A unique method for interfacial SIMS studies has been reported. Utilizing this system, it is possible to directly observe DCPI formation by monitoring the  $[M_{\text{PHE}} + \text{D}]^+$  signal at the interface of an isotopically enriched and non-enriched film. The mechanism of  $[M_{\text{PHE}} + \text{D}]^+$  formation will be similar to  $[M + \text{H}]^+$  ion formation in a film of either PHE or PHE- $\text{D}_8$  and possibly in other similar organic films.

This method can also be extended to investigate fundamentals of depth profiling due to the limited perturbation of a system by isotopic enrichment. Many common organic analytes can be obtained commercially or synthesized with varying degrees of enrichment. Inserting an isotopic marker at specific sites on a molecule can help tailor experiments to probe fundamental questions incurred for depth profiling studies. This protocol should also be useful for elucidating the details of ionization during gas cluster ion bombardment where the chemical damage is smaller, and the ion beam mixing effects are reduced further.

## Acknowledgements

The authors acknowledge financial support from the National Institute of Health under Grant 2R01 EB002016-18, the National Science Foundation under Grant CHE-0908226 and the Department of Energy under Grant DE-FG02-06ER15803. Barbara Garrison and Andreas Wucher are also acknowledged for their contributions in data interpretation and presentation.

## References

- [1] P. D. Piehowski, M. E. Kurczy, D. Willingham, S. Parry, M. L. Heien, N. Winograd, A. G. Ewing, *Langmuir* **2008**, *24*, 7906–7911.
- [2] C. Lu, A. Wucher, N. Winograd, *Surf. Interface Anal.* **2011**, *43*, 81–83.
- [3] T. P. Roddy, D. M. Cannon, S. G. Ostrowski, A. G. Ewing, N. Winograd, *Anal. Chem.* **2003**, *75*, 4087–4094.
- [4] B. J. Garrison, *Surf. Interface Anal.* **2011**, *43*, 134–136.
- [5] D. Willingham, D. A. Brenes, A. Wucher, N. Winograd, *J. Phys. Chem. C* **2010**, *114*, 5391–5399.
- [6] D. Willingham, D. A. Brenes, N. Winograd, A. Wucher, *Surf. Interface Anal.* **2011**, *43*, 45–48.
- [7] D. Willingham, A. Kucher, N. Winograd, *Appl. Surf. Sci.* **2008**, *255*, 831–833.
- [8] R. M. Braun, *Rapid Commun. Mass Spectrom.* **1998**, *12*, 1246.
- [9] J. Cheng, A. Wucher, N. Winograd, *J. Phys. Chem. B* **2006**, *110*, 8329–8336.