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Mechanism for Increased Yield with SF_5^+ Projectiles in Organic SIMS: The Substrate Effect

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Experiments have shown that the use of polyatomic projectiles in secondary ion mass spectrometry (SIMS) increases the secondary yield of molecular ions by an order of magnitude or more. This observation, coupled with the availability of an SF_5^+ source, has sparked renewed interest in SIMS measurements for characterizing a wide range of molecules. In this paper, we present the results of molecular dynamics simulations with Xe and SF_5 projectiles that show that the molecular ion yield from bombarded organic surfaces is enhanced by the use of polyatomic projectiles. The model systems consist of a monolayer of twenty biphenyl molecules on two different substrates, Cu(001) and Si(100), and are designed as a prototype for experimentally studied systems. Our results show that the structure of the lattice is the critical factor. The breakup of the SF_5 cluster within the more open lattice of the Si(100) substrate initiates collision cascades that lead to substrate atoms hitting the biphenyl molecules from below, which results in a greater yield of ejected molecules. The results are important because they predict that the nature of the substrate or matrix is a critical factor in maximizing the molecular ion yield.

Bombardment of organic surfaces by keV polyatomic projectiles has been observed to increase the yield of desorbed molecular ions by an order of magnitude or more.[1–5] This observation, coupled with the availability of an SF_5^+ source, has sparked renewed interest in secondary ion mass spectrometry (SIMS) measurements for characterizing a wide range of molecules.[6–8] The most dramatic enhancements have been observed by Kotter and Benninghoven, who measured the yield on bulk and spin-coated polymer surfaces with 10 keV Ar^+, Xe^+, and SF_5^+ ions and found yield increases up to 1000 times greater with the polyatomic projectile.[6] Although more frag-

mentation was observed with the polyatomic projectile, the damage cross section was found to increase less than the corresponding yield. Smaller increases in yield of a factor of 2 or so have been observed on samples of organic monolayers on metallic substrates.[3b,7]

The prevailing rationalizations of the observed enhancement of the molecular desorption yield focus on the relative geometry and structure of the incoming projectile. For example, the energy deposited by SF_5^+ is thought to be distributed over a broader region of the surface than an isobaric atomic species such as Xe^+. The constituent cluster atoms then initiate their own low-energy overlapping collision sequences, leading to a greater number of ejected molecules. Here we show that although this

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TABLE 1: Yield of Ejected Stable Biphenyl Molecules out of 150 Trajectories[a]

substrate	Xe	SF_5	ratio
Cu(001)	200	248	1.2
Si(100)-(2 × 1)	163	362	2.2
^{12}Cu(001)	124	264	2.1
^{12}Si(100)-(2 × 1)	94	363	3.9

[a] The ratio of the yield with the SF_5 projectile to the yield with the SF_5 projectile is calculated.

picture is generally accurate, it is a unique coupling between the structure of the lattice and the incident projectile that determines whether cluster bombardment provides a meaningful improvement in the information content of the mass spectrum. Our model is developed with molecular dynamics simulations of SF_5 and Xe bombardment of a biphenyl layer adsorbed to the surface of different types of substrates. The calculations are made possible by blending many-body and pairwise additive interaction potentials which have been shown to yield accurate predictions of the response of an organic film to ion bombardment.[9] The simulations show that the enhancement of desorption is observed when the cluster breaks apart beneath the surface layer, leading to more efficient upward momentum transfer with surface molecules. The results predict that the greatest enhancements will be found for polyatomic projectiles impinging on highly open lattices, and that more dense metallic-like substrates will be less effective at enhancing the molecular yield.

The model systems consist of a monolayer of twenty biphenyl molecules on two different substrates, Cu(100) and Si(100), and are designed as a prototype for experimentally studied systems. Xe and SF_5, which have similar masses, are used as the bombarding particles in order to examine the effect of increasing the number of particles in the projectile. Details of similar calculations, including the interaction potentials, have been described previously,[10,11] and further details will be published elsewhere.[12] The Cu(100) microcrystallite consists of 2574 atoms with nine layers of 286 atoms, and the Si(100)-(2 × 1) microcrystallite consists of 2016 atoms with nine layers of 224 atoms. The emission yield with each projectile is calculated by averaging over a set of trajectories, where each trajectory has a different impact point on the surface. The bombarding particles, Xe and SF_5, are aimed normal to the surface with 0.60 keV of kinetic energy. Using a higher kinetic energy would require a larger crystallite and considerably more computer time. We have, however, performed sample calculations using 10 keV incident kinetic energy and the conclusions reached below are qualitatively identical. For each set of 150 trajectories, the number of stable biphenyl molecules is determined as the number of whole, ejected biphenyl molecules with 0−10 eV of internal energy. Simulations on other organic layers on metal surfaces have shown that it is necessary to estimate which molecules will unimolecularly dissociate before reaching the detector and eliminate them from the analysis.[9b,f,g]

The yield of ejected stable biphenyl molecules out of 150 trajectories for Xe and SF_5 on each substrate and the ratio of the yield with SF_5 to that with Xe are shown in Table 1. In both cases, the yield with the cluster is greater than the yield with the monatomic projectile. By comparing the ratio of the yield with SF_5 to that with Xe, however, it is apparent that the increase in yield is twice as much for the Si(100)-(2 × 1) substrate than for the Cu(001) substrate. This difference could be due to two factors: the lighter mass of the Si substrate atoms and/or the lattice structure of Si(100). Simulations were performed on the copper and silicon substrates in which the mass of the substrate atoms was changed to that of carbon, and
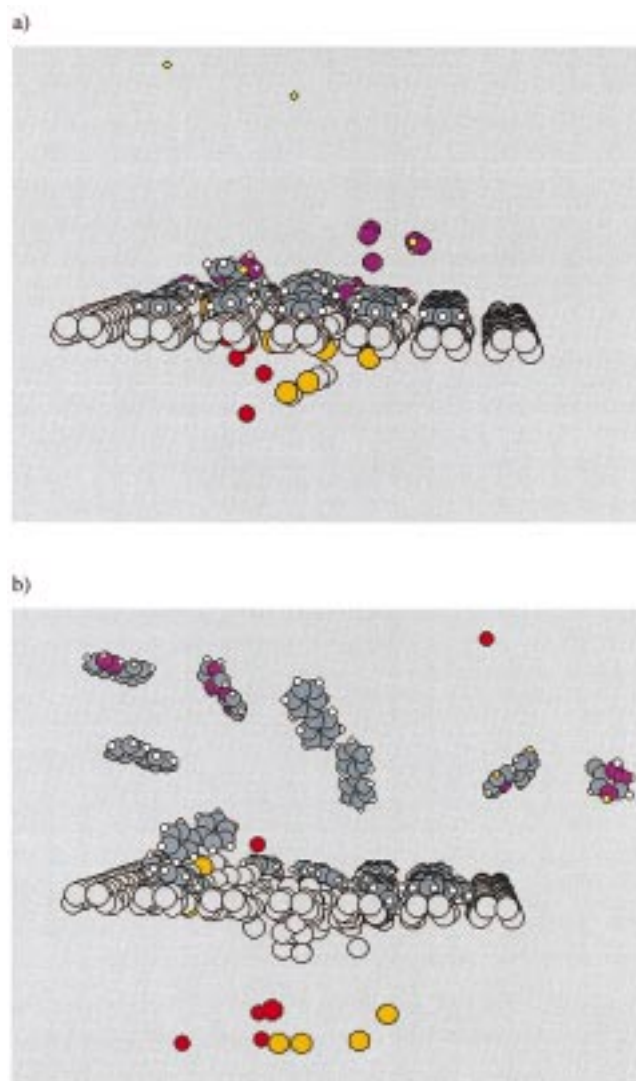

Figure 1. Example of a trajectory calculated for 0.60 keV SF_5 bombardment of $C_{12}H_{10}$/Si(100)-(2 × 1). Side view looking down along the dimer rows. To highlight the incoming cluster, only the top layer of silicon atoms is shown. The incoming SF_5 is red. Atoms with kinetic energies greater than 0.5 eV are colored. (a) Penetration and dissociation of SF_5 cluster. (b) Resulting action from impact. Five stable biphenyl molecules and two damaged biphenyl molecules are ejected.

these substrates are referred to as ^{12}Si(100) and ^{12}Cu(001). For both of the mass 12 substrates the yield with the Xe projectile decreases, whereas the SF_5 yield remains the same. Most important, though, is the result that the increase in yield with SF_5 compared to Xe is two times greater for the ^{12}Si(100) substrate than for the ^{12}Cu(001) substrate, indicating that the structure of the lattice is the critical factor. The calculated enhancements are somewhat smaller than reported by experiment.[1−8] This difference could be because the experiments are performed on a bulk organic solid, while the simulations are performed on a monolayer of organic material.

We are able to elucidate the atomistic mechanisms responsible for the increase in yield by using the results of the molecular dynamics simulations to create animations that show how the atoms move with time as the particle bombardment proceeds. For the close-packed Cu(001) surface, the SF_5 breaks apart as it hits the surface and is reflected toward the vacuum. Collision cascades can be generated in the top layer of the surface that result in the ejection of molecules and fragments.[13] With the Si(100)-(2 × 1) substrate, on the other hand, the entire SF_5

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projectile is able to penetrate the surface and break apart within the substrate as shown in Figure 1a. The breakup of the SF_5 cluster within the lattice initiates collision cascades that lead to substrate atoms hitting the biphenyl molecules from below, which results in upward movement of the molecules toward the vacuum. Consequently, as shown in Figure 1b, more biphenyl molecules are ultimately ejected.

The results presented here are important because they predict that the nature of the substrate or matrix is a critical factor in maximizing the molecular ion yield. For dense substrates, where the projectile cannot effectively reach the second layer before breaking apart, the cluster sources are predicted to be less effective. For more open lattices, however, the projectile initiates multiple collision cascades beneath the organic layer, leading to a greater number of ejected intact molecules than when the cluster projectile decomposes on impact. This result is good news for future SIMS experiments. The open character of a bulk polymer matrix affords an ideal structure for efficient energy absorption of polyatomic projectiles, and enhancement should indeed be very large. Moreover, experiments on biological cells where the matrix is a frozen hydrated mixture should be greatly aided by the use of these projectiles. In fact, preliminary experiments have shown that SF_5^+ improves the analysis of polymers and biological samples.[6,14-15] Of particular interest would be the development of polyatomic ion beams that can be focused for molecule-specific imaging experiments where sensitivity is presently the limiting factor.

References and Notes

(1) (a) Appelhans, A. D.; Delmore, J. E. *Anal. Chem.* **1989,** *61*, 1087–1093. (b) Groenewald, G. S.; Delmore, D. E.; Olson, J. E.; Appelhans, A. D.; Ingram, J. C.; Dahl, D. A. *Int. J. Mass Spectrom. Ion Processes* **1997**, *163*, 185–195. (c) Groenewold, G. S.; Gianotto, A. K.; Olson, J. E.; Appelhans, A. D.; Ingram, J. C.; Delmore, J. E.; Shaw, A. D. *Int. J. Mass Spectrom. Ion Processes* **1998**, *174*, 167–177.

(2) (a) Blain, M. G.; Della-Negra, S.; Joret, H.; Le Beyec, Y.; Schweikert, E. A. *Phys. Rev. Lett.* **1989**, *63*, 1625–1628. (b) Benguerba, M.; Brunelle, A.; Della-Negra, S.; Depauw, J.; Joret, H.; Le Beyec, Y.; Blain, M. G.; Schweikert, E. A.; Ben Assayag, G.; Sudraud, P. *Nucl. Instrum. Methods* **1991**, *B62*, 8–22.

(3) (a) Van Stipdonk, M. J.; Harris, R. D.; Schweikert, E. A. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 1987–1991. (b) Harris, R. D.; Van Stipdonk, M. J.; Schweikert, E. A. *Int. J. Mass Spectrom. Ion Processes* **1998**, *174*, 167–177.

(4) (a) Boussofiane-Baudin, K.; Bolbach, G.; Brunelle, A.; Della-Negra, S.; Hakansson, P.; Le Beyec, Y. *Nucl. Instrum. Methods* **1994**, *B88*, 160–163. (b) Le Beyec, Y. *Int. J. Mass Spectrom. Ion Processes* **1998***, 174*, 101–117.

(5) (a) Mahoney, J. F.; Perel, J.; Ruatta, S. A.; Martino, P. A.; Husain, S.; Lee, T. D. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 441–445. (b) Mahoney, J. F.; Parilis, E. S.; Lee, T. D. *Nucl. Instrum. Methods* **1994**, *B88,* 154–159.

(6) Kotter, F.; Benninghoven, A. *Appl. Surf. Sci.* **1998**, *133*, 47–57.

(7) Ada, E. T.; Hanley L. *Int. J. Mass Spectrom. Ion Processes* **1998**, *174*, 231–244.

(8) Hand, O. W.; Majumdar, T. K.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1990**, *97*, 34–45.

(9) (a) Taylor, R. S.; Garrison, B. J. *J. Am. Chem. Soc.* **1994**, *116*, 4465–4466. (b) Taylor, R. S.; Garrison, B. J. *Langmuir* **1995**, *11*, 1220–1228. (c) Taylor, R. S.; Brummel, C. L.; Winograd, N.; Garrison, B. J.; Vickerman, J. C. *Chem. Phys. Lett.* **1995**, *233*, 575–579. (d) Taylor, R. S.; Garrison, B. J. *Chem Phys. Lett.* **1994**, *230*, 495–500. (e) Taylor, R. S.; Garrison, B. J. *Int. J. Mass Spectrom.* **1995**, *143*, 225–233. (f) Chatterjee, R.; Postawa, Z.; Garrison, B. J.; Winograd, N. *J. Phys. Chem B.* **1999**, *103*, 151–163. (g) Liu, K. S. S.; Yong, C. Y.; Garrison, B. J.; Vickerman, J. C. *J. Phys. Chem.*, in press.

(10) Smith, R.; Harrison, D. E., Jr.; Garrison, B. J. *Phys. Rev.* **1989**, *B40*, 93–101.

(11) (a) Zaric, R.; Pearson, B.; Krantzman, K. D.; Garrison, B. J. *Int. J. Mass Spectrom. Ion Processes* **1998***, 174*, 155–166. (b) Zaric, R.; Pearson, B.; Krantzman, K. D.; Garrison, B. J. In *Secondary Ion Mass Spectrometry, SIMS XI*; Lareau, R., Gillen, G., Eds.; New York: John Wiley and Sons: New York, 1998; pp 601–604.

(12) Townes, J. A.; White, A. K.; Krantzman, K. D.; Garrison, B. J., manuscript in preparation.

(13) The mechanism for ejection of an intact molecule was elucidated in our previous simulations, which are cited in ref 9.

(14) Gillen, G.; Roberson, S. *Rapid Commun. Mass Spectrom.* **1998**, *12*, 1303–1312.

(15) Todd, P. J.; McMahon, J. M.; McCandlish, C. A., Jr. In Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Spring, CA, June 1–5, 1997.