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International Journal of Mass Spectrometry 212 (2001) 467–475

www.elsevier.com/locate/ijms

Desorption ionization/processes

Molecular desorption and secondary ion mass spectrometry

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Received 7 May 2001; accepted 30 July 2001

Abstract

Experiments and molecular dynamics computer simulations have been conducted to gain insight into the mechanism of desorption of molecules on surfaces subjected to bombardment by energetic particles. The model system is a monolayer of benzene on Ag{111}. The computer simulations are performed using a many body potential function based on the Brenner potential. This function allows interactions between desorbing benzene molecules to be accurately modeled. The experiments utilize multiphoton resonance ionization of desorbed benzene molecules to determine energy, angle, and vibrational state-selected information. The results show there is close agreement between the model and the measurements, providing a confirmation that the physical basis of the calculations, are indeed correct. The benzene molecules are desorbed by direct collisions with substrate atoms and many of the molecules are internally excited enough to be in excited vibrational levels or to undergo fragmentation. For multilayers of benzene on a metal, the desorbed molecules have much lower kinetic energy, suggesting that exothermic chemical reactions in the film may play a role in producing a thermal-like event. The results also show that the excited molecules arise mainly from the surface layer since molecules originating from below the surface tend to be cooled by multiple collisions with other molecules in the interfacial region. The model calculations are extended to show that cooperative uplifting of surface molecules is observed even for species of molecular weight of several thousand Dalton. The context of these experiments and calculations is considered as a consequence of a vision of the mechanism of molecular desorption in secondary ion mass spectrometry presented 20 years ago by Cooks. (Int J Mass Spectrom 212 (2001) 467–475) © 2001 Elsevier Science B.V.

Keywords: Molecular dynamics; SIMS; Molecular desorption; Ion bombardment; Benzene

1. Introduction

The fact that organic molecules can be enticed to desorb from solids by various stimulated processes whose energy greatly exceeds that of chemical bonds remains somewhat of an enigmatic observation. The phenomenon has been studied for nearly twenty-five years with experimental configurations beginning using energetic particles (secondary ion mass spectrometry (SIMS) [1], fast atom bombardment [2], and plasma desorption mass spectrometry) and extending to matrix-assisted laser desorption ionization (MALDI) [3]. One of the first attempts to unify the various experimental observations associated with

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Dedicated to R. Graham Cooks on the occasion of his sixtieth birthday.

PII S1387-3806(01)00510-3

molecular desorption is attributable to Pachuta and coworkers [4]. Using a combination of knowledge about the physics of particle-surface interactions, a unique perspective on organic mass spectrometry, and an uncanny intuition, this group emphasized three important processes that might contribute to the desorption of molecular species. These included (1) energy deposition by the primary particle that ultimately transfers enough kinetic energy to the target molecule to allow it to desorb, (2) ion/molecule reactions that occur in the interfacial region that lead to species detectable by the mass spectrometer, and (3) unimolecular decay of internally excited molecules as they move toward the detector [5]. It is particularly noteworthy that in one of the early experimental examples of molecular desorption of an amino acid, Cooks made the first reference to cationization of these molecules, underpinning idea (2) previously [6].

Although much is known about the qualitative aspects of molecular desorption, breakthroughs in our understanding of molecular desorption on an atomic level have remained elusive, presumably due to the complex nature of the dynamics. This problem is even more pressing today as the applications of SIMS have continued to expand toward surface analysis and especially toward molecule-specific imaging experiments [7] where sub-micron spatial resolution is now possible. Moreover, advances in MALDI, where molecular desorption mechanisms could have some overlap with those found for SIMS; continue to pave new roads in biological chemistry. Better theory is still urgently needed in both arenas.

Our goal has been to provide this long-sought picture using molecular dynamics (MD) computer simulations to determine the trajectories of atoms that comprise the desorbing molecule and to coordinate the predictions of these calculations with experiments on similar systems. Here we focus on desorption of simple aromatic molecules adsorbed in various coverage amounts on a metal surface. This class of molecules is important since we have been able to develop an interaction potential function that allows us to examine all three of the Cooks processes by molecular dynamics [8]. Moreover, for the simplest molecules such as benzene, laser techniques may be employed to probe the population of various spectroscopic states such that issues related to translational energy, internal energy, and stability may be compared with predictions of the models [9]. It is remarkable that the spectroscopy is sensitive enough to characterize just a fraction of a monolayer of these molecules. These systems are also amenable to the study of chemical reactions in the interfacial region and to the determination of the influence of any chemical bond between the adsorbate and the surface on the desorption yield [10].

Our results show that the molecular dynamics is yielding information very close to that found in the laboratory for low coverage of benzene on silver. The models clearly reveal the presence of a cooperative uplifting of the adsorbate by moving substrate atoms, usually associated with high action points sampled by the primary particle [11]. High action points result when the primary particle induces the motion of a large number of substrate atoms near the target surface. Moreover, many of the benzene molecules are found to desorb with more than enough internal energy to decompose on the way to the detector. These effects are strongly dependent upon the number of benzene molecules adsorbed on the surface, showing that collisions between molecules and interaction between the molecules and the surface dramatically influence the trajectory [9]. Finally, we show that for multilayer films of benzene that most of the internally excited molecules originate from the surface layer and not from within the bulk of the film. In general, the three processes proposed by Cooks twenty years ago still guide our thinking in developing atomic-level descriptions of the molecular desorption event. These proposals have proven to be remarkably prescient and invaluable guideposts for both experimentalists and theoreticians.

2. Calculation methods

Molecular dynamics calculations consist of integrating Hamilton's equations of motions over time to determine the position and velocity of all particles

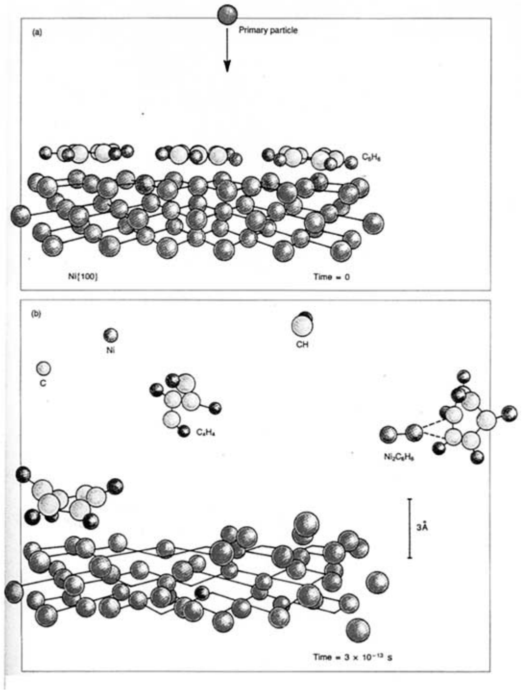

Fig. 1. Molecular dynamics computer simulations of benzene molecules desorbed from a nickel surface covered with a monolayer of benzene. The primary particle is shown in red, nickel atoms are green, carbon atoms are yellow, and hydrogen atoms are black. The blue atoms are nickel atoms that become part of a cluster. From [13].

during the ion-bombardment event. The final positions and momenta are used to calculate a number of experimental observables such as total yield, and energy and angular distributions. With a few assumptions it is also possible to infer information about cluster formation and the distribution of internal energy within the cluster [11]. This analysis allows some predictions of vibrational and rotational spectra [12].

The key component needed to acquire accurate MD results is to utilize reliable interaction potential functions. During the time that Cooks was developing his models of molecular desorption, the sophistication of these functions for organic molecules was very low. The results of our first calculations for benzene are reproduced in Fig. 1 [13,14]. The calculations utilized purely pair-wise additive interaction functions and did not allow for reactions between benzene molecules. Although the potentials were relatively simple, the results show that the collision cascade of metal substrate atoms is clearly capable of desorbing the molecule intact, that fragmentation is induced by collisions at the surface and that substrate metal ions may strongly interact with the desorbing molecule (cationization?). The time scale of the event is found to occur in less than a picosecond, suggesting the process occurs much faster than simple thermal desorption. In the early days, however, it was not possible to make quantitative predictions associated with these qualitative pictures. Moreover, the detail in experimental data was lacking for these comparisons.

During recent years, there have been dramatic advances in the development of interaction potentials for MD simulations. For benzene, we now model the interactions using a many-body potential developed by Brenner [15]. This formulation allows for chemical reactions and accompanying changes in atomic hybridization during the course of a reaction. A deficiency of this potential is the neglect of long-range van der Waals type interactions that impacts our ability to study some effects due to collisions between molecules. This deficiency has recently been removed [16], and our new approach should allow accurate modeling of bombarded multilayer molecular films [17]. To complete the picture of benzene adsorbed onto a metal substrate, an MD/Monte Carlo corrected effective medium potential is utilized to describe the Ag–Ag interactions [8]. This function reproduces the energy and angular distributions of ejected metal atoms very accurately. The benzene molecules are attached to the metal surface using a pair-wise additive Lennard–Jones potential. The parameters are selected to yield a reasonable binding energy. A Moliere function is used to describe the collisions between the primary particle and the substrate. This assumption is based on the fact that the primary particle imparts energy and momentum to the system and does not play a direct role in the chemistry of the bombardment process. Finally, high-speed computer power now allows the size of the model microcrystallite to be dramatically increased. In some cases, trajectories for thousands of atoms have been employed.

3. Experimental methods

Laser techniques have been developed to measure the trajectories of desorbed molecules [10]. These techniques are favored since they are well-suited to performing energy and angular distribution measurements of neutral molecules in specific spectroscopic states. Detection is achieved by choosing a wavelength resonant with a specific transition and ionizing using multiphoton absorption. Although the mechanistic scheme proposed by Cooks was developed for secondary molecular ions, we feel that it is important to decouple the ionization step from the desorption step to simplify the problem as much as possible. Moreover, this approach allows a much more direct comparison with the predictions of the MD calculations. The details of the experimental setup have been described in several previous papers and will not be reviewed here [8,18].

For these experiments, molecules are dosed onto a substrate that has been cleaned by ion-bombardment, annealed, and cooled to 120 K [12]. For benzene, a liquid sample is subjected to several freeze-pump-thaw cycles and the vapor is then introduced into the vacuum chamber at a specific pressure for a predetermined amount of time. In our situation, a 7 L exposure (1 Langmuir $= 1 \times 10^{-6}$ Torr s) corresponds to a monolayer coverage, where one monolayer corresponds to 0.146 molecules/Ag atom. For most of the aromatic molecules, ionization is achieved by focusing the laser to a ribbon shape about 1 cm above the crystal surface. Nonresonant ionization is achieved using the 4th harmonic of the Nd:YAG laser at 266 nm. Resonant ionization of benzene is achieved by tuning the frequency-doubled output of the Nd:YAG-pumped dye laser to drive the $6^1{}_0$ transition at 259.01 nm originating from the zero level of the molecular ground state, and the $6^0{}_1$ transition at 266.82 nm starting from the first quantum of the v''_6 vibration.

The angle of incidence of the primary ion beam is 45° and the neutral molecules ejected normal to the surface are detected within an angular range of ±20°. The time distributions are obtained after integrating 50 laser shots at each delay time. The measurements are made under static conditions and the primary ion dose is kept below 10^{12} ions/cm^2 in all experiments. These conditions are such that it is unlikely that the same spot will be impacted more than once.

4. Results and discussion

4.1. Benzene monolayers on Ag{111}

Will it be possible to make a direct connection between experimental results and MD simulations for an organic overlayer? This is the central question for our research effort since an answer in the affirmative allows us to utilize the microscopic information embedded in the computer printouts to glean unprecedented information about the details of the desorption event. Benzene makes a convenient model since, as noted previously, accurate many-body potential functions are available and the molecule is large enough to undergo most of the reaction sequences in the model put forth by Cooks. Moreover, the calculations may logically be extended to larger molecules consisting of aromatic subunits in order to identify the important mechanisms for desorption of bigger molecules.

Perhaps the most important result associated with the benzene study is shown in Fig. 2. The experimental kinetic energy (KE) distribution of benzene molecules peaks at about 1.14 eV, and the intensity drops off rapidly with KE reaching zero at about 7 eV. The distribution is obtained using nonresonant ionization at 266 nm, suggesting that the plot represents a sum of both ground state and excited state benzene molecules. The MD simulations mimic this response extremely well, reproducing both the peak position and the general shape of the falloff. There is a small deviation at higher kinetic energies where the simulations predict measurable intensity to about 12 eV. Presumably, these molecules undergo unimolecular decay on the way to the detector and are never counted. It is difficult to imagine that such close agreement between experiment and model could be achieved if the basic physics associated with the MD calculations were in significant error.

The general shape of this curve differs significantly

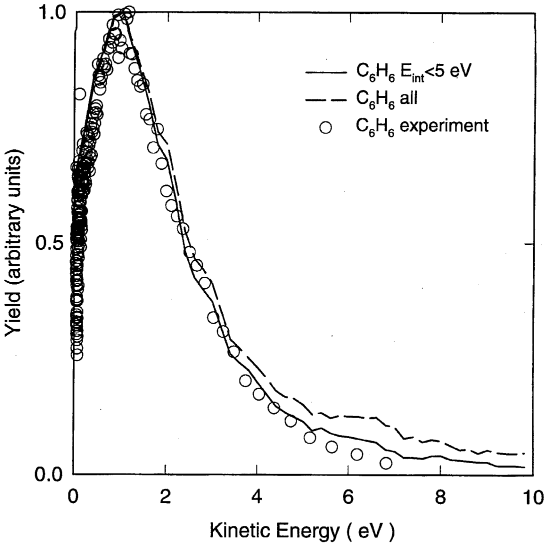

Fig. 2. Calculated and experimental KE distributions of benzene desorbed from a (3 × 3) benzene overlayer on Ag{111}. The calculations were performed using 500 eV Ar+ ions, and the experiments were carried out using 8 keV Ar+ ions. The two calculated curves show the difference between the KE distribution of all particles and those whose total internal energy is less than 5 eV. From [8].

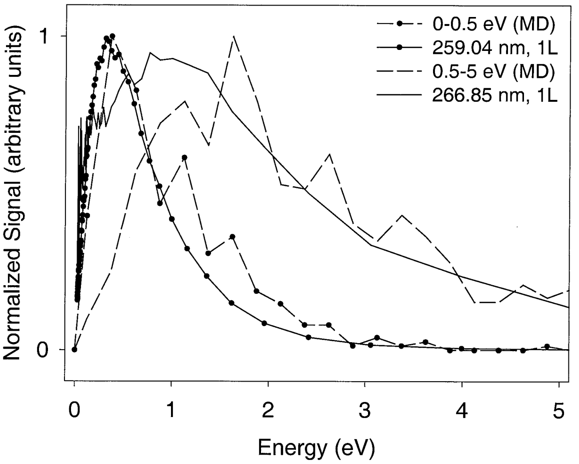

Fig. 3. Calculated and experimental KE distributions of benzene desorbed from a (3 × 3) benzene overlayer on Ag{111}. Here, the different experimental distributions are acquired from the ground state and a vibrationally excited state of benzene. The calculated distributions are sorted to reflect those molecules with low internal energy and higher internal energy. The range selected is a compromise between the experimental value of the vibrational level, and the number of calculated trajectories in that range that yield adequate statistical accuracy.

from the KE distribution of metal atoms desorbed from crystal surfaces. Those distributions are approximated by the Thompson equation [19] and are characterized by a maximum intensity at the value of one-half of the surface binding energy, followed by a decrease in intensity that follows KE^{-2}. The more rapid falloff shown in Fig. 2 arises in part from the fact that higher energy collisions tend to fragment the benzene molecule, removing intensity from the high-energy tail.

It is possible to refine further the measurements and calculations to include specific vibrational states. For benzene, the ground vibrational level is probed using 259.01 nm photons, and there is a vibrational excited state that is 0.08 eV above the ground state that is probed using 266.82 nm photons [20]. The calculations can be roughly compared to experiments by sorting all molecules that possess the lowest internal energy from those that possess the highest values. The KE distributions obtained from applying this procedure are shown in Fig. 3. Note that the shape of these kinetic energy distributions is quite similar to the generic shape shown in Fig. 2, although the excited molecules have, on average, higher translational KE than the ground state.

What is the origin of this excitation and how can it be controlled? There are clues from the dependence of the KE distributions on the amount of deposited benzene. As the number of benzene layers is increased, the peak in the KE distribution is observed to shift toward much lower values (<0.05 eV) [9,12]. This result suggests that the nature of the collision cascade in a molecular film is much different from that found in a metal substrate. We believe this observation suggests that exothermic chemical reactions in concert with a high density of molecular collisions allow for a more thermal-like desorption event. Vibrationally excited molecules, however, exhibit a KE peak that is lower than the ground state peak [12]. A possible explanation for this observation is that in thick layers only the first few collisions between an escaping substrate silver atom and an adsorbate benzene molecule are energetic enough to excite the molecule. Before this excited molecule can be detected, it has to travel through the overlayer where intermolecular collisions are abundant. Collisional quenching or unimolecular decomposition is thus probable. Such effects would not be expected for ground state molecules. This effect supports the original Cooks proposal of a soup of reactions occurring between vibrationally and/or electronically excited molecules in the "selvedge" interfacial region. Molecular dynamics simulations of multilayer films are being initiated with the new long range potential in order to directly quantify these effects [17].

We can directly test the idea that excited molecules originate mainly from the top layer by examining the influence of an inert buffer layer of sec-butyl alcohol (sBA) deposited directly on top of the benzene monolayer as shown in Fig. 4. The alcohol was chosen for this purpose since it is similar in size to a benzene molecule and it does not produce any mass fragments that might interfere with the detection of benzene. The KE distributions reveal that the presence of this inert layer much more effectively reduces the yield of excited state molecules than of ground state molecules.

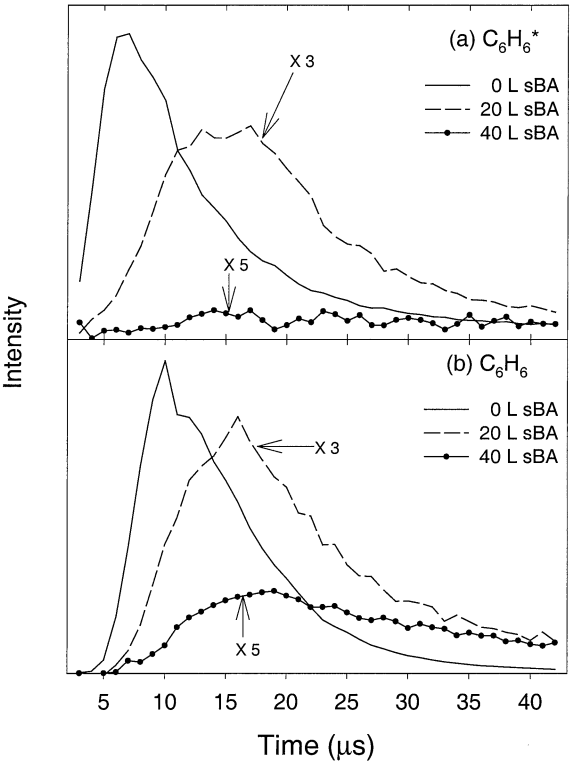

Fig. 4. Experimental KE distributions of excited state (a) and ground state (b) benzene desorbed from a (3 × 3) benzene overlayer and covered with the indicated exposure of sBA. The solid line represents the intensity of the benzene with no overlayer present. The ground state intensity is about an order of magnitude larger than the excited state intensity. Note the x axis is given in time units instead of energy units simply for graphical clarity.

And finally, it is interesting to follow the trajectories of ejecting Ag atoms as they push their way through the benzene overlayer. This type of study is particularly appealing since results can be compared to energy and angular distributions from clean metal surfaces. As reported previously, a substantial number of Ag atoms are found to be sputtered into a metastable electronically excited state ($4d^9 5s^2$) that lays 3.75 eV above the ground state. The yield of atoms in this excited state is found to decrease rapidly as the amount of benzene covering the surface of the crystal is increased [12]. Also, the KE and polar angle distributions are modified after applying benzene to the surface. For both Ag and Ag*, the KE distributions tend to decay more rapidly and shift to lower energies with increasing benzene coverage. A large fraction of Ag* atoms are quenched by the presence of the benzene overlayer. The polar angle distributions broaden significantly and shift toward the direction normal to the surface. The MD simulations for the Ag atoms agree quantitatively with these measurements. All of these observations point to the fact that silver atoms undergo collisions with the adsorbed benzene molecules. Moreover, the larger size of Ag* increases its likelihood of colliding with benzene molecules. As a result of the larger collision cross-section coupled with collision-induced deexcitation, the trends for Ag* are exaggerated relative to those observed for ground state Ag.

4.2. Cooperative uplifting and bigger molecules

Perhaps the most important consequence of the case study of the molecular desorption of ion-bombarded benzene is that through the interplay of experiment and MD simulations, a consistent picture of at least one system is beginning to emerge. With the confidence that the modeling approach is a valid one, it seems logical to extend the calculations to examine desorption of higher molecular weight systems. For example, it is feasible to examine molecules with many aromatic subunits using the same potential energy functions prescribed for the benzene system. This approach opens the possibility of exploring the mechanistic reasons behind the ejection of large molecules.

The system investigated is sec-butyl terminated polystyrene (PS) tetramers (MW = 474 Da) adsorbed on an Ag surface [11]. We have found in approximately 25% of the trajectories of Ar bombardment at 5 keV that high action in the substrate correlates with a high yield of particles being ejected. The highest total ejected mass observed in our simulations is close to 10 kDa, i.e. the upper mass limit of ejected species in SIMS. The mechanism for molecular liftoff is a cooperative uplifting in which several Ag atoms underneath the organic molecules move toward the vacuum at approximately the same time. In order to test these ideas on larger molecules, we have devised a slightly different configuration in which several of the PS tetramers are replaced by PS hexadecamers (16 repeat units, molecular weight ~2000 Da using the tritium isotope in the simulations) as shown in Fig. 5(a). In order to reproduce a high action event, the central PS tetramer was left in place. The analysis of the trajectory indicates that the early development of the collision cascade in the Ag crystal is very similar to the one with PS tetramers. At 200 fs, a few single Ag atoms are emitted and a collective motion including several tens of Ag atoms begins under the top right PS hexadecamer as shown in Fig. 5(b). After 700 fs, a large protrusion is created by the correlated motion of these atoms, pushing the PS oligomer upward. In the same time, the bottom left PS molecule is smoothly lifted up, although the action in that part of the top silver layer is less apparent. The two PS molecules should not decompose on the time scale of SIMS analysis according to Rice-Ramsperger-Kassel (RRK) theory [21]. It appears quite clear that the collective motions are the key to high sputtering yields of intermediate size molecules.

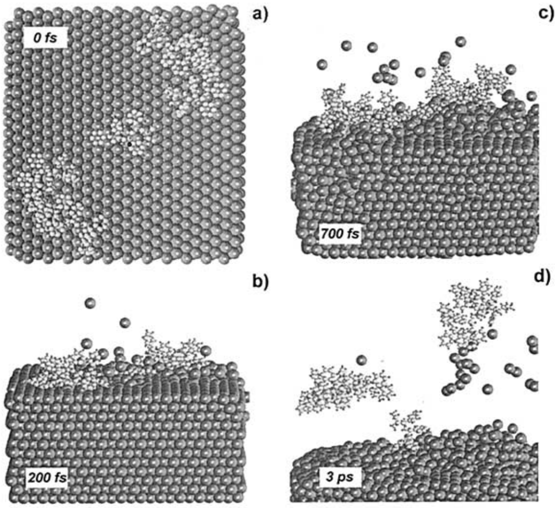

Fig. 5. Emission of two polystyrene hexadecamers induced by a 5 keV Ar atom aimed at a high action point on the surface. The times are indicated on each panel. From [11].

4.3. Matrix effects and the influence of surface covalent bonds

In Cooks' vision of molecular desorption and SIMS, he suggested a number of matrix effects which might potentially enhance the yield of secondary ions. As a matter of fact, he often advocated the addition of ion-promoters to the sample in a fashion not unlike that ultimately used with MALDI experiments [22]. Another matrix effect that was not considered by the Cooks model involves chemical binding between the desorbing molecule and the substrate. This effect was first examined by Taylor et al. [23] using a simple hydrocarbon chain model system. Their results showed that by increasing the strength of the covalent bond between the hydrocarbon and the metal that the yield of molecules not only decreases, but that the degree of fragmentation of the chain increases dramatically. Moreover, the fragments appeared to arise preferentially from the top of the chain.

From a practical point of view, this chemical effect is extremely important and impacts a number of ongoing SIMS experiments. We have been interested in characterizing peptide and related molecules that are chemically linked to polystyrene spheres [24].

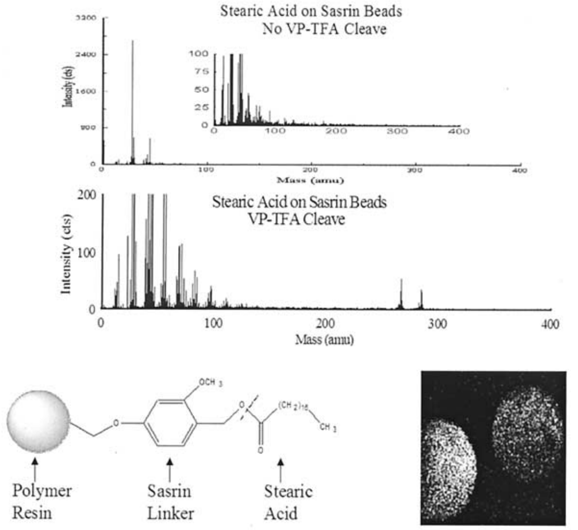

Fig. 6. Illustration of the effect of surface covalent bonds on the SIMS spectrum of surface-bound molecules. The top panel shows the spectrum of stearic acid linked to a polystyrene resin using the coupling scheme shown below. The second panel shows the spectrum of the bead surface after exposure to a vapor phase trifluoroacetic acid treatment. A SIMS image of two beads around *m/z* 285, the molecular weight of protonated stearic acid, indicates that the stearic acid remains localized on the bead.

This construct is utilized in the synthesis of large combinatorial libraries of molecules used for the discovery of lead drugs. An example of the effect is shown in Fig. 6. In this case, stearic acid is linked to the bead via an ester linkage as indicated in the figure and the bead is imaged using a scanning ion beam probe. The resulting mass spectrum consists mainly of fragment ions, and gives virtually no specific information about the surface chemistry. When the covalent bond is broken by exposure to a gas of trifluoroacetic acid, however, the molecular ion is readily observed. This simple procedure clearly makes an enormous difference in the quality of the result and is understood on the basis of the earlier MD simulations.

5. Conclusions

We have attempted to provide a detailed view of the important atomic motion that leads to molecular desorption stimulated by ion bombardment. The picture we have described using well-defined model systems has emerged from the results of computer simulations and from experiments that can be properly compared to these calculations. Although there are still missing pieces, our vision of the process is closely tied to the Cooks mechanistic view, and in many ways has been derived from it. For example, he always challenged our models as being inadequate to describe organic systems. And it is perhaps this challenge that has driven us to push forward in this direction. The focus now is to provide as detailed a view of molecular multilayers as we now have for molecular monolayers. Will it be possible to describe a molecular collision cascade with all the energetic processes outlined by Cooks? We believe the tools exist for this to happen.

In the ensuing years, Professor Cooks has moved away from the SIMS field, but his experiences there have obviously influenced his experiments in soft landing and surface induced dissociation. In the meantime, MALDI has certainly become the technique of choice for the mass spectrometric identification of large molecules. And it is interesting to note that closely related MD simulations have successfully provided a great deal of insight into the laser ablation process as well. With SIMS, however, the applications continue to expand and the need for more detailed understanding of the mechanisms of molecular desorption remain. The recent discovery that cluster ion beams can improve the yield of molecular ions by several orders of magnitude, and the continuing possibility of molecule-specific imaging with focused ion beams are just two of the emerging areas. Whatever the future, however, the imprint left by the Cooks' contributions will be much appreciated for years to come.

Acknowledgements

The authors appreciate the support of the NIH, NSF, and the Office of Naval Research for partial support of this work. We also appreciate the contributions of Chad Meserole, Rob Braun, Reema Chatterjee, Erno Vanderweert, Arnaud Delcourt, and Zbigniew Postawa to the ideas and results presented here.

References

[1] A. Benninghoven, W.K. Sichtermann, Anal. Chem. 50 (1978) 1180.
[2] M. Barber, R.S. Bordoli, R.D. Sedgwick, A.N. Tyler, J. Chem. Soc., Chem. Commun. (1981) 325.
[3] F. Hillenkamp, M. Karas, R.C. Beavis, B.T. Chait, Anal. Chem. 63 (1991) 1193A.
[4] S.J. Pachuta, R.G. Cooks, Chem. Rev. 87 (1987) 674.
[5] S.J. Pachuta, R.G. Cooks, in Desorption Mass Spectrometry, P.A. Lyon (Ed.), ACS Symposium Series 291, ACS Washington, DC, 1985, p. 1.
[6] H. Grade, R.G. Cooks, N. Winograd, J. Am. Chem. Soc. 99 (1977) 7725.
[7] M.L. Pacholski, N. Winograd, Chem. Rev. 99 (1999) 2977.
[8] R. Chatterjee, Z. Postawa, N. Winograd, B.J. Garrison, J. Phys. Chem. B 103 (1999) 151.
[9] R. Chatterjee, D.E. Riederer, Z. Postawa, N. Winograd, J. Phys. Chem. 102 (1998) 4176.
[10] D.E. Riederer, R. Chatterjee, S.W. Rosencrance, Z. Postawa, T.D. Dunbar, D.L. Allara, N. Winograd, J. Am. Chem. Soc. 119 (1997) 8089.
[11] A. Delcorte, B.J. Garrison, J. Phys. Chem. B 104 (2000) 6485.
[12] E. Vandeweert, C.A. Meserole, A. Sostarecz, N. Winograd, Z. Postawa, Nucl. Instrum. Methods Phys. Rev. B. 164/165 (2000) 820.
[13] Focus, Anal Chem. 59 (1987) 588A.
[14] B.J. Garrison, J. Am. Chem. Soc. 102 (1980) 6553.
[15] D.W. Brenner, Phys. Rev. B 42 (1990) 9458.
[16] S.J. Stuart, A.B. Tutein, J.A. Harrison, J. Chem. Phys. 112 (2000) 6472.
[17] K.D. Krantzman, Z. Postawa, B.J. Garrison, N. Winograd, S.J. Stuart, J.A. Harrison, Nucl. Instrum. Methods Phys. Res. B, in press.
[18] P.H. Kobrin, G.A. Schick, J.P. Baxter, N. Winograd, Rev. Sci. Instrum. 57 (1986) 1354.
[19] M.W. Thompson, Philos. Mag. 18 (1968) 377.
[20] J.H. Callamon, T.M. Dunn, I.M. Mills, Philos. Trans. R. Soc. London, Ser. A 269 (1966) 499.
[21] A. Delcorte, X. Vanden Eynde, P. Bertrand, J.C. Vickerman, B.J. Garrison, J. Phys. Chem. B 12 (2000) 2673.
[22] K.L. Busch, B.H. Hsu, Y.-X. Xie, R.G. Cooks, Anal. Chem. 55 (1983) 1157.
[23] R.S. Taylor, C.L. Brummel, N. Winograd, B.J. Garrison, J.C. Vickerman, Chem. Phys. Lett. 233 (1995) 575.
[24] C.L. Brummel, I.N. W. Lee, Y. Zhou, S.J. Benkovic, N. Winograd, Science 264 (1994) 399.