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Molecular ionization probability in cluster-SIMS

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The ionization efficiency of molecular species sputtered under bombardment with cluster ion beams is generally assumed to be rather low, but hard experimental evidence for this notion is still lacking. In order to estimate the prospects for possible sensitivity improvements in molecular secondary ion mass spectrometry (SIMS) experiments, the author therefore reports on recent experiments utilizing laser postionization (LPI) in order to determine an absolute ionization probability value for a few organic molecules sputtered under C₆₀ cluster ion bombardment. The results show that the molecular ionization efficiency obtained under these bombarding conditions is of the order of 10⁻³, leaving at least 2 orders of magnitude for possible enhancement of the physical or a chemical ionization mechanism leading to the formation of (quasi-) molecular secondary ions. Analyzing the measured molecular LPI signal, the author demonstrates that about the same headroom exists for improvement of the currently achieved postionization efficiency. Using trehalose as a model system, the author then illustrates the level of improvement achieved by different attempts to utilize projectile induced surface chemistry in order to enhance the ionization efficiency. The results may be useful to guide new developments aimed at enhancing the detection sensitivity in molecular cluster-SIMS experiments.

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I. INTRODUCTION

Current state-of-the-art approaches to molecular secondary ion mass spectrometry (SIMS) involve the use of cluster projectiles in order to reduce the bombardment induced fragmentation and damage accumulation at the sample surface.^{1,2} In these experiments, one of the key factors limiting sensitivity is the ionization efficiency of sputtered molecular species.³⁻⁵ Although many published applications have successfully utilized small, rather unspecific fragment ions to identify certain molecular species in the investigated sample system,⁶ it is principally desirable to enhance molecular specificity by detecting (quasi-) molecular ions that represent either the intact parent molecule itself or at least larger molecule specific fragments. The ionization efficiency of such species in the course of the emission event is generally assumed to be rather low,³ with values down to the order of 10⁻⁵ being sometimes quoted in the literature.^{7,8} However, it is rarely reported how these estimates have been obtained, so that the actual value—and even the order of magnitude—of molecular ionization efficiencies must still be considered to be practically unknown. While it is relatively straightforward to measure the useful molecular ion yield, i.e., the number of intact (quasi-) molecular ions detected per molecule equivalent of material removed from a molecular sample, one must realize that this quantity represents a convolution of fragmentation, ionization, and detection probability of a sputtered molecule. In order to judge the prospects for possible sensitivity enhancement via improvements of physical or chemical ionization mechanisms, it is of utmost interest to unravel these factors and quantitatively determine the ionization probability of the different species ejected from the surface at least to an accuracy of its order of magnitude. Ultimately, this task requires the mass resolved detection of sputtered *neutral* species along with their

ionized counterparts, a technique currently termed secondary neutral mass spectrometry (SNMS). This paper will report on recent combined SIMS/SNMS experiments utilizing laser postionization (LPI) in order to determine a reliable estimate of an absolute ionization probability value for a few organic molecules sputtered under C₆₀ cluster ion bombardment. The results will be interpreted in terms of the possible gain in sensitivity, which could be achieved by improving the ionization efficiency. Then, we will briefly review a few recent attempts to utilize projectile induced surface chemistry in order to enhance the ionization efficiency of sputtered molecules, a strategy which turns out to be particularly important in cases where (rare) gas cluster ion beams (GCIB's) are used to generate the measured SIMS signal. For trehalose as a model system, we will illustrate the level of improvement which is currently obtained using reactive gas cluster projectiles. In addition, we will analyze published useful yield data obtained for this system under different bombarding conditions in order to extract information about the variation of the ionization efficiency as a function of experimental parameters such as nature, size, composition, and energy of the projectile clusters. The results may be useful to guide new developments aimed at enhancing the detection sensitivity in molecular cluster-SIMS experiments.

II. EXPERIMENTAL METHODOLOGY

In the remainder of this paper, the ionization probability (or efficiency) of a sputtered species *X* is defined as

$$\alpha_X^{+,-} = \frac{Y_{X^{+,-}}}{Y_X} = \frac{Y_{X^{+,-}}}{Y_{X^0} + Y_{X^+} + Y_{X^-}}, \quad (1)$$

where Y_X is the partial sputter yield of species *X* regardless of its charge state, while $Y_{X^{+,-}}$ and Y_{X^0} denote the partial sputter yields of positively and negatively charged secondary ions

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X^+ , X^- , and neutrals X^0 , respectively. The experimental ionization probability data reproduced in this paper have been acquired using different time-of-flight (ToF) mass spectrometers, which have been described in detail in the respective cited publications. Some of the systems are well documented commercial instruments such as TOF-SIMS V (IonTof GmbH) or J105 (Ionoptika, Ltd.), while other experiments used home-built instruments such as the BioToF system developed jointly at the Pennsylvania State and Manchester Universities. All systems are equipped with different cluster ion sources delivering metal, fullerene, or gas clusters such as Bi_3^+ , C_{60}^+ , or Ar_n^+ , respectively, which were used for acquisition of mass spectral SIMS data at mass resolution ranging from ~ 1000 to $\sim 10\,000$.

Experiments using postionization of sputtered neutral molecules were performed using pulsed laser photoionization in combination with a BioToF-type mass spectrometer. Here, two different strategies were employed in order to deliver efficient, but “soft” photoionization while minimizing laser induced photofragmentation. The first approach involves nonresonant single photon ionization using vacuum ultraviolet radiation generated, for instance, using an F_2 excimer laser. While the photon flux density delivered by such a laser is high enough to drive the photoionization process into saturation, thereby gaining important information about the postionization efficiency, the wavelength of 157 nm naturally limits the number of accessible molecules to those with ionization energies below the respective photon energy of about 8 eV. The second approach involves strong field photoionization, where an ultrashort infrared laser pulse is focused to such high intensity that the laser field becomes comparable to the coulomb field binding the valence electrons. Also in this case, it was demonstrated that intact photoionization of sputtered molecules is possible with saturated efficiency, albeit in a fairly small effective ionization volume due to the tight focusing conditions. In this context, “saturation” of the photoionization process denotes a situation where a further increase of the laser intensity does not increase the measured photoion signal any more. It is a common assumption in photoionization theory that this corresponds to unit ionization probability, i.e., all target atoms irradiated by the postionization laser are being ionized.⁹ Particularly if a nonresonant absorption/ionization scheme is employed, there is no physical reason why an irradiated particle should not be affected by the laser light. For atoms, this means that all irradiated particles will eventually be ionized once the laser intensity is sufficiently high. Depending on the laser intensity, there will be a distribution of the resulting ionization charge states, and therefore one may define the total photoionization probability by summing over all charge states of the resulting ions. For molecules, the situation is more complicated due to the possibility of laser induced fragmentation, which will be discussed in more detail below.

The reflectron-type mass spectrometer employed in these experiments is used in delayed extraction mode and tuned in such a way that secondary ions and postionized neutrals are detected from the same effective “sensitive” volume located at distances between 0.5 and 1 mm above the sample surface.

As described in detail elsewhere,¹⁰ this ensures comparable detection efficiency for secondary ions and their postionized neutral counterparts, thereby directly permitting a determination of their ionization probability from the signal ratio measured with and without the ionization laser being fired. As a necessary prerequisite, it must be ensured that the postionization laser intersects the entire plume of sputtered neutral particles in order to facilitate a quantitative comparison with the detected secondary ion signal. While this condition is relatively easy to fulfil in the single photon ionization experiments using the 157 nm F_2 laser, it is impossible to illuminate the entire sensitive volume with the tightly focused laser used in the strong field ionization scheme. In this case, the laser beam is therefore scanned through the detectable plume of sputtered neutral particles, and the signal is integrated in order to determine the total postionization signal. Details of this procedure are found in the respective publications.^{11–14}

An important feature of all experimental data quoted in this paper is the fact that the experiments described earlier are sensitive to the *number density* of sputtered neutral particles within the sensitive volume rather than their *flux*. Partial sputter yields entering Eq. (1), on the other hand, represent the flux of sputtered particles. To interpret the experimental data in terms of the ionization probability, it is important to note that the emission velocity distributions of sputtered ions and neutrals may in principle be different, leading to a different conversion from measured density to flux. A detailed discussion of this effect indicates that the possible uncertainty introduced into the determination of $\alpha^{+,-}$ is probably of the order of a factor two.^{11,12}

III. IONIZATION MECHANISM

During the past three decades, various models describing the ionization of a sputtered particle in the course of its emission from the bombarded surface have been published in the literature. The present paper is not intended to provide a comprehensive review of those, which can be found in a number of published reviews on the topic.^{15–20} Here, we concentrate on some fundamentals which are essential to understand the experimentally observed trends, particularly for sputtered molecules.

In principle, the different ionization mechanisms encountered in current molecular SIMS experiments can be coarsely divided into *physical* and *chemical* ionization processes. The physical basis for the first class is schematically depicted in Fig. 1 for positive (upper panel) and negative (lower panel) ionization. The theoretical description is based on resonant electron transfer processes, and the ultimate charge state of the sputtered particle is determined by calculating the occupation probability of its valence states at infinite distance from the surface.¹⁶ Critical quantities in this context are the surface work function Φ and the ionization energy I of the outgoing particle, where note must be taken that the valence level depends on the particle’s distance from the surface. For positive ionization, it is obvious that the predicted α^+ must

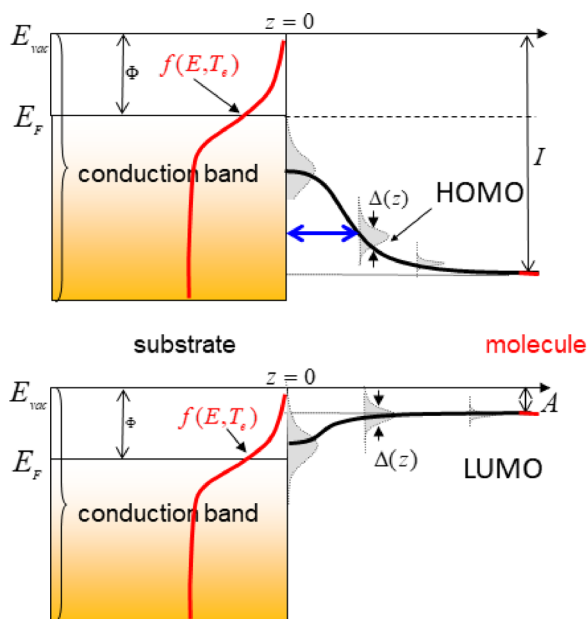


FIG. 1. (Color online) Schematic energy diagram for positive (upper panel) and negative (lower panel) ionization of a sputtered molecule.

decrease with increasing difference $I - \Phi$, a dependence which is often parametrized as

$$\alpha^+ \propto \exp\left(-\frac{I - \Phi}{\varepsilon}\right), \quad (2)$$

with a similar relation

$$\alpha^- \propto \exp\left(-\frac{\Phi - A}{\varepsilon}\right), \quad (3)$$

holding for negative ionization. It should be noted, however, that the scaling according to Eq. (3) has recently been questioned by Wittmaack.²¹

The nature of the proportionality constant in Eqs. (2) and (3), as well as the characteristic energy ε , is debated in the literature, and many different models describing the dependence of ε on, for instance, the (electronic) surface temperature and the velocity of the outgoing particle exist.¹⁹

A fundamentally different ionization mechanism involves a chemical reaction between a sputtered neutral molecule M and some radical $R^{+,-}$ carrying the charge. Prominent examples for such a process are *protonation* or *cationization* leading to the formation of quasimolecular complexes like $[M+H]^+$, $[M+Na]^+$, or $[M+Ag]^+$. In a similar way, negative adduct ions like $[M+O]^-$, $[M+OH]^-$, or $[M+Cl]^-$ can be formed, provided the required ionic radicals are present in the vicinity of a sputtered molecule. Cationization via a bond to a positive metal ion represents an ubiquitous ionization pathway in cases where molecular monolayers are deposited on a metal substrate.²² For thicker molecular samples, alkali adduct ions formed from salt impurities in the film are often observed in the positive ion spectrum. In the context of cluster ion beams, probably the most interesting quasimolecular ions are the protonated and deprotonated

molecules $[M+H]^+$ and $[M-H]^-$, respectively. The former can either be formed by addition of free proton radicals generated in the sputtering event or as the result of a more complicated reaction scheme involving, for instance, H_3O^+ or NH_3^+ . Deprotonation, on the other hand, may occur via abstraction reactions involving, for instance, OH^- or NO_3^- radicals. In any case, the necessary condition for such a mechanism to be efficient is that the required reactands are present either directly at or in the selvedge immediately above the surface exactly at the time needed to react with a sputtered molecule.

IV. EXPERIMENTAL OBSERVATIONS

As outlined in Sec. I, the purpose of this paper is to present a short review of the current state of knowledge regarding the ionization efficiency of molecular species sputtered under bombardment with cluster ions beams. This section is therefore organized as follows: First, we will present the results of recent experiments where laser postionization was used to arrive at a quantitative estimate of the ionization probability for a few selected sputtered molecules. Second, we present a brief description of the relevant ionization mechanisms and then present a short summary of some recent efforts aimed at enhancing the molecular ionization efficiency. For the particular case of trehalose as a model system, we then compile measured useful ion yield data extracted from published experiments using different—reactive or nonreactive—cluster ion projectiles and analyze the results in terms of possible enhancements of the ionization efficiency via projectile induced surface chemistry.

A. Ionization probability measurements

Probably the first quantitative measurements of molecular ionization probabilities were performed for inorganic clusters sputtered from various metal and semiconductor surfaces under bombardment with monoatomic rare gas ions.^{23–31} In these experiments, saturated single photon postionization was employed, and the value of α_M^+ was derived from a direct comparison of measured SIMS and SNMS signals. An example is shown in the upper panel of Fig. 2, which depicts the ionization probability measured for In_n clusters sputtered from a polycrystalline indium surface under bombardment with small gold cluster ions. The data were measured using a home-built reflectron ToF spectrometer in combination with the single photon postionization scheme described earlier.³² For comparison, similar data taken under bombardment with polyatomic fullerene cluster ions are shown in the bottom panel, which were taken on a BioToF instrument in combination with strong field photoinionization.¹³ The data displayed in Fig. 2 are interesting because they allow to study the variation of α_M^+ as a function of the size of the sputtered molecule M in a systematic way. For all projectiles, a similar trend is observed, where the ionization probability increases with increasing cluster size n from small values typical for atomic secondary ions ($n = 1$) sputtered from a clean metal surface to values of several 10^{-2} for larger clusters. Moreover, the ionization efficiency appears to level off and reach a plateau

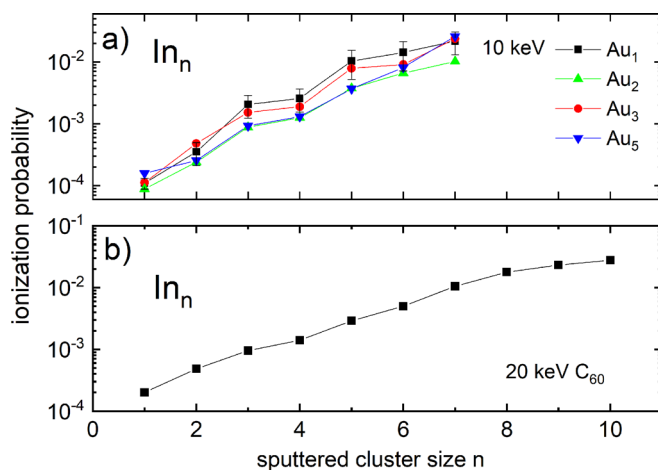


FIG. 2. (Color online) Ionization probability of indium clusters sputtered from a polycrystalline indium surface under bombardment with (a) 10 keV Au_m^+ (Ref. 32), and (b) 20 keV C_{60}^+ ions (Ref. 13). The data displayed in the bottom panel were reproduced with permission from Breuer *et al.*, J. Phys. Chem. A **118**, 8542 (2014). Copyright 2014, American Chemical Society.

if the sputtered molecule contains more than about ten atoms. These findings have been reproduced for clusters sputtered from a number of different target materials and must therefore be regarded as typical for the sputtering process of inorganic molecules.³³ They are in principle consistent with the physical ionization mechanism described earlier, since the ionization energy of a sputtered cluster tends to decrease with increasing size (ranging from the atomic I at $n = 1$ to the bulk work function at $n \rightarrow \infty$). Therefore, the observed increase of α^+ along with its leveling off at large values of n is principally expected, but nevertheless the measured data cannot quantitatively be reproduced by Eq. (2).

Comparable data for organic molecules have long been missing due to the fact that these species are rapidly destroyed under bombardment with monoatomic projectiles. In addition, photofragmentation represents a severe problem for the quantitative determination of molecular ionization probabilities, since the postionization efficiency must be known in order to arrive at an absolute value of $\alpha^{+,-}$. Only recently, Popczun *et al.*^{11,12} have managed to acquire experimental data on the absolute value of α^+ for some selected molecules. In these experiments, strong field photoionization was used in conjunction with C_{60}^+ bombardment of molecular films deposited on a silicon substrate. Sputtered intact neutral molecules M were monitored via the laser induced molecular ion signal $[M]^+$, and the amount of photofragmentation was examined by comparison with data taken on gas phase molecules generated by thermal evaporation. Since the latter are produced with negligible internal energy, they should provide a lower limit to the laser induced fragmentation probability of sputtered molecules which may be emitted in higher internally excited states. An upper limit of the fragmentation probability was determined by relating the signal of intact molecules to that detected for all fragments in the spectrum of postionized sputtered neutral species. This way, the survival probability of a sputtered neutral molecule against fragmentation upon photoionization

could be bracketed, thereby allowing to quantitatively determine the ionization probability of emitted intact parent molecules to within one order of magnitude accuracy. In order to investigate secondary ions formed by different ionization mechanisms, two exemplary cases were studied. In the first case, sputtering of a coronene film results in the formation of molecular secondary ions $[M]^+$, where M denotes the intact parent coronene molecule, possibly indicating a physical ionization mechanism for these species. In this case, the ionization efficiency can be directly determined using Eq. (1) by comparing the $[M]^+$ signal measured in the SIMS and SNMS spectra, respectively. Bombardment of a guanine film, on the other hand, results in the production of protonated or deprotonated molecules, which dominate the molecular spectra and thereby clearly indicate a chemical ionization mechanism for these species. In this case, the (positive) ionization probability was determined by relating the $[M+H]^+$ secondary ion signal to that of $[M]^+$ resulting from postionization of neutral molecules $[M]$. In both cases, it was found that the ionization efficiency of a sputtered intact molecule is of the order of several 10^{-3} . For coronene, the experiment has been reproduced using the single photon postionization approach,³⁴ resulting in a slightly larger α^+ value which, however, still resides in the regime of several 10^{-3} . These results indicate that there is headroom of about 2 orders of magnitude for sensitivity improvement in molecular cluster SIMS via enhancement of the ionization efficiency.

B. Ionization efficiency enhancement

Possible ways to enhance the ionization efficiency depend on the prevailing ionization mechanism. The physical ionization process described earlier may in principle be enhanced by electronic excitation of the surface at the point in space and time from which a sputtered molecule is emitted. In fact, one of the existing microscopic models describing secondary ion formation relies on a local, transient excitation, rendering the characteristic energy in Eqs. (2) and (3) as $\varepsilon = kT_e$, where T_e represents a temporally enhanced electronic temperature of the emitting substrate. Under kilo-electron-volt ion impact, it was demonstrated that relatively high values of T_e may be transiently reached via kinetic excitation caused by electronic stopping of all particles set in motion by the collision cascade. In order to enhance the excitation level, one may, in principle, think of using multiply charged projectile ions, which become neutralized upon impact, thereby additionally depositing their potential (ionization) energy into the electronic system. An alternative way to create even more electronic excitation is to use high energy projectile ions, which deposit their kinetic energy mostly via electronic stopping. For the particular example of coronene molecules, we have recently tried this route using 1 GeV Au^{26+} projectile ions generated at the GSI Helmholtz Centre of Heavy Ion Research in Darmstadt, Germany. Using the same SIMS/SNMS strategy as explained earlier, in combination with the single photon postionization scheme, a value of 1×10^{-2} was measured for α_M^+ under these conditions,³⁵ representing a moderate enhancement by about

a factor 2 with respect to that observed under 20 keV C_{60}^+ bombardment using the same experimental setup.

In order to enhance the chemical ionization mechanism, it is clear that the number of required radical reactands driving the ionization reaction must be increased. Moreover, this enhancement must be synchronized with the emission process, so that the radicals are created exactly at the point in space and time where and when a sputtered molecule is emitted. Following the same route as applied for decades in inorganic SIMS, one may envision to use the projectile ion beam itself in order to modify the surface chemistry in a way that is favorable for secondary ion formation. Along this line, projectiles like Cs^+ or O_2^+ are routinely used to enhance the negative or positive ionization efficiency of sputtered atoms. For the particular case of cluster SIMS, these considerations suggest to use the projectile cluster in order to modify the chemistry right in the impact zone from where the sputtered material originates. This appears to be particularly important in molecular SIMS applications, where rare-gas GCIB are often employed, which are relatively easy to generate but generally produce a relatively low ionization efficiency. One possible strategy to enhance the protonation efficiency is to dope the rare gas clusters with a chemically reactive species capable to deliver free proton radicals upon impact and dissociation. Using this method, we have demonstrated moderate enhancement effects for dopant molecules like CO_2 , CH_4 , or HCl , with the magnitude of the enhancement being of the order of a factor two.^{36,37} However, if the HCl -doped argon cluster projectile is combined with an adsorbed H_2O surface layer which may, for instance, be generated via water vapor flooding during the GCIB bombardment, the HCl molecules supplied by the projectile become chemically reactive and act to significantly enhance the protonation efficiency.³⁷ For trehalose as a model system, it was demonstrated that the efficiency of $[M+H]^+$ ion formation can be enhanced by more than 1 order of magnitude using this method as shown in Fig. 3.³⁷

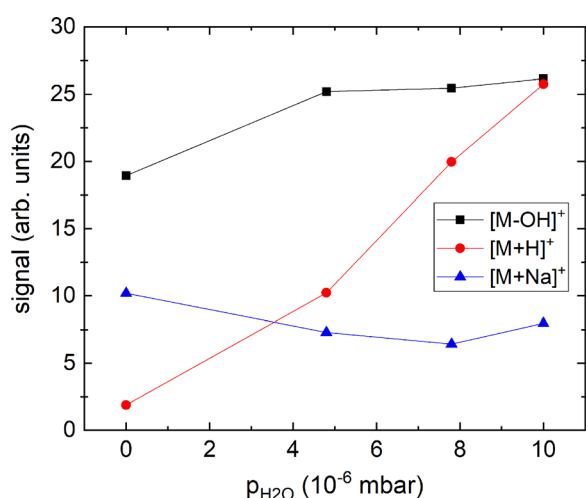


Fig. 3. (Color online) Molecule specific SIMS signals measured on a trehalose film under dynamic reactive ionization conditions using an HCl -doped 20 keV Ar_{2000} cluster ion beam and simultaneous flooding with water vapor vs H_2O partial pressure in the analysis chamber. The data were taken on a J105 instrument and reproduced from Tian *et al.*, J. Am. Soc. Mass Spectrom. **27**, 285 (2015).

Another possible strategy is to entirely replace the rare gas cluster projectiles with molecular clusters such as $(CO_2)_n$,³⁸ $(CH_4)_n$ (Ref. 39) or $(H_2O)_n$.^{8,40–42} For the trehalose system, the result obtained with a water cluster ion beam is shown in Fig. 4. It is seen that the protonation efficiency can be enhanced by about 2 orders of magnitude upon switching from Ar_n to $(H_2O)_n$, with a sweet spot for most efficient enhancement being observed at an impact energy of about 3 eV per H_2O molecule.^{42,43}

In both cases depicted in Figs. 3 and 4, the projectile induced surface chemistry was shown to boost the formation of protonated molecules $[M+H]^+$ – which is normally a minor signal in the spectra measured for trehalose as shown in Fig. 5 – to the same level as the most prominent $[M-OH]^+$ fragment which is commonly observed as the major molecule specific ion signal for this system.

A third possible strategy to enhance molecular ionization probabilities is by cationization or anionization.²² For organic monolayers deposited on a metal surface, ionization of desorbed intact molecules often occurs via $[M+Me]^+$ adduct ion formation with substrate metal atoms Me . This “substrate cationization” represents an intriguing molecular ionization process, since the respective ionization efficiency was found to be much less dependent on molecule properties than for any other ionization mechanism.²² For thicker samples, surface metallization has been demonstrated to (moderately) enhance the ionization efficiency of some samples, but mostly via enhancement of the $[M+H]^+$ ion yield and rarely via $[M+Me]^+$ adduct ion formation.⁴⁴ The yield enhancement observed for atomic projectiles in these “Metal-assisted SIMS” experiments, however, is not found under bombardment with cluster ion beams.⁴⁵ On the other hand, a prominent ionization pathway, particularly

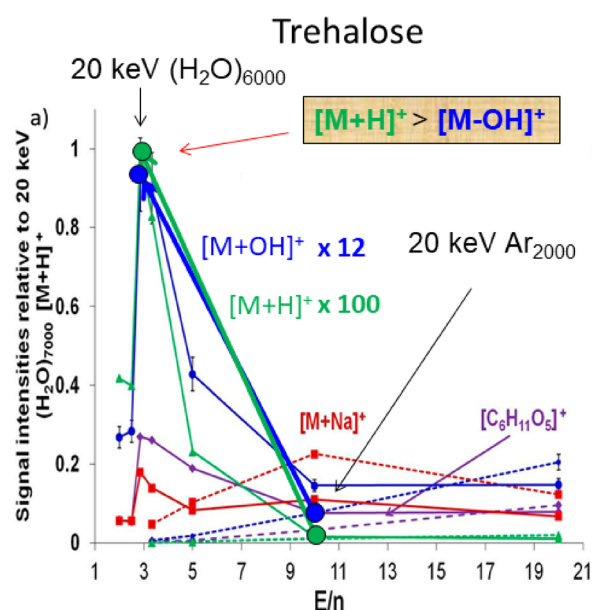


Fig. 4. (Color online) Molecule specific SIMS signals measured under bombardment of a trehalose film with Ar_n and $(H_2O)_n$ cluster ion beams of different impact energy per cluster constituent (Ar atom or H_2O molecule). The data were taken on a J105 instrument and reproduced with permission from Rabbani *et al.*, Anal. Chem. **87**, 2367 (2015). Copyright 2015, licensed under a Creative Commons Attribution (CC-BY).

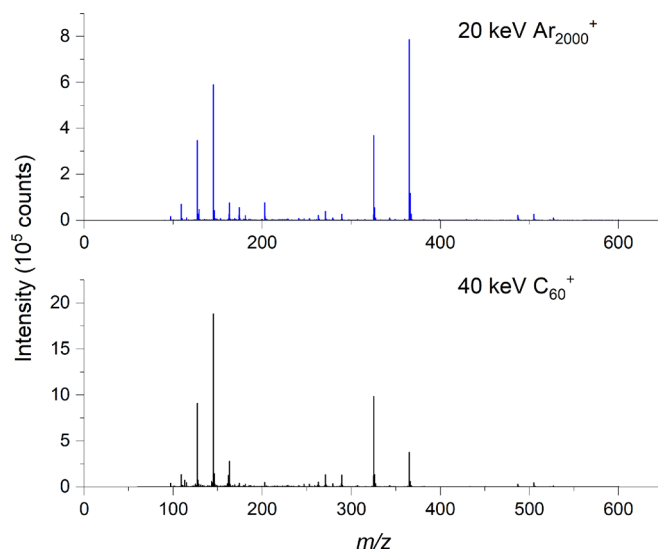


Fig. 5. (Color online) Positive secondary ion mass spectra measured on a trehalose film deposited on Si under bombardment with 40 keV C_{60}^+ (upper panel) and 20 keV Ar_{2000}^+ cluster ion projectiles (data courtesy of Hua Tian).

for polar molecules, is the formation of alkali adduct ions such as $[M+Na]^+$ or $[M+K]^+$.⁴⁶ In a similar way, anionization via halogen adduct ion formation such as $[M+F]^-$ or $[M+Cl]^-$ may also work as an efficient ionization pathway for the formation of negative quasimolecular ions. For the specific example of trehalose, spurious remnants of salt in the molecular film often lead to a prominent $[M+Na]^+$ adduct ion formation. In fact, this signal is often found to dominate the quasimolecular ion spectrum for this system,⁴⁷ as seen for the spectrum generated by a 20 keV Ar_{2000}^+ cluster ion beam in Fig. 5. If NaCl salt is deliberately added to the solution used to produce the film, one finds signal saturation for concentrations at the percent level as shown in Fig. 6. Under these conditions, the production efficiency of $[M+Na]^+$ becomes larger than that found for $[M+H]^+$ formation under optimized projectile induced surface chemistry conditions, while the $[M-OH]^+$ and $[M+H]^+$ signals are slightly suppressed. These observations are identical to those made by Lu *et al.*⁴⁸ under 40 keV C_{60} bombardment, who found the total ionization efficiency of a sputtered trehalose molecule to be enhanced by salt addition, while that of a peptide molecule embedded in the trehalose film shows the opposite trend, namely, a decrease by about an order of magnitude, thereby clearly indicating the dependence of this ionization mechanism on the nature of the molecule. At the same time, the formation of trehalose $[M+Cl]^-$ ions is observed with comparable efficiency as $[M-H]^-$, and the signal levels of protonated and deprotonated molecules are also comparable. For the specific trehalose system investigated here, these findings indicate that there might be a limit as to which extent the ionization efficiency of a sputtered intact trehalose molecule can be enhanced by tuning the surface chemistry.

C. Useful molecular ion yield

In order to judge the prospects of possible sensitivity enhancements in molecular SIMS via projectile induced

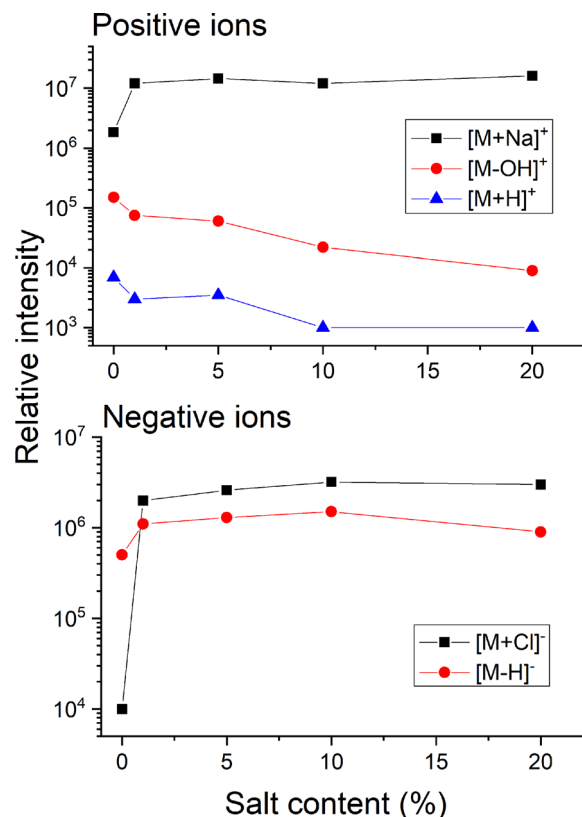


Fig. 6. (Color online) Molecule specific SIMS signals measured on a trehalose film with added sodium chloride vs concentration of NaCl added to the solution from which the film was spin cast. The data were taken on a J105 instrument using a 20 keV Ar_{2000} GCIB (Ref. 37).

chemistry, it is of interest to compare useful yields of molecule specific ions obtained under different bombardment conditions. The trehalose system discussed here is well suited for such a comparison because it has been used as one of the standard platforms for testing concepts of molecular SIMS and molecular depth profiling between different laboratories. We therefore chose to analyze published data measured on this system and determine the useful yield τ as the number of detected molecular ions per molecule equivalent of material removed from the surface. This definition eliminates the sputter yield from the measured signal, which may be vastly different between different projectiles. However, it should be noted that the useful yield defined this way contains other contributions besides the ionization efficiency. For a (quasi-)molecular ion, τ can formally be written as

$$\tau = p_{surv} \cdot \alpha^{+,-} \cdot T, \quad (4)$$

where p_{surv} denotes the survival probability of a molecule against fragmentation in the course of the sputtering process and T denotes the collection and detection efficiency for the emitted secondary ion. Analyzing data from different publications, it needs to be taken into account that the data may have been acquired on different instruments. There are several consequences of this fact, the first being a possible difference in the value of T , which will be discussed below.

Useful yield values were then determined as follows. First, only data were analyzed where absolute values of the

integrated signals along with the ion fluence used to produce the measured spectra were given. In view of the fact that some publications reported sputter depth profiles while other only contained static spectral data measured at the pristine surface, we decided to compare the signal measured at the *beginning* of a depth profile instead of the steady-state signal. In order to acknowledge the different detection schemes used in different instruments (analog detection in the J105 instrument versus single ion counting in other systems), the signal levels reported in “cts” from a J105 instrument were corrected for the fact that a “ct” does not represent the registration of one ion but rather denotes an arbitrary bit value delivered by the transient digitizer recording the signal. In order to determine the number of actually detected ions, the integrated mass peak area must therefore be divided by the peak integral produced by a single ion, which has been measured to be of the order of 70 cts under typical operating conditions.⁴⁹ For other ToF systems using single ion counting, the reported peak integral was directly interpreted as the number of detected ions.

In order to calculate the number of projectiles used to generate the measured spectra, the reported ion fluence was multiplied by the ion beam raster area used during spectrum acquisition. The resulting number was multiplied by the total sputter yield, which was either taken from the respective publication itself (if it was determined and provided therein) or calculated using the universal equation.⁵⁰ Volume sputter yields given in nm³ of sample removed per projectile impact were converted into the number of sputtered molecule equivalents using the density of 2.7 molecules/nm³ of trehalose. The useful yield was then calculated as the ratio between detected ions and sputtered molecule equivalents. The resulting values are listed in Table I. The reason for three different columns being displayed for C₆₀ projectiles is that the data were acquired on different instruments and with different kinetic impact energy. As indicated in Table I, all data obtained with gas cluster ion beams were taken with a J105 chemical imager. In order to be comparable, the fifth column therefore displays values for C₆₀ projectiles that were determined on this instrument as well. The data presented in columns 1 through 4, on the other hand, were obtained with more conventional ToF spectrometers such

as the TOF-SIMS V or BioToF instruments, respectively. The useful yield values displayed in columns 4 and 5 were obtained in the same laboratory under identical bombardment conditions (40 keV C₆₀⁺ impinging under 45° with respect to the surface normal), and the difference between the measured useful yield values must therefore be attributed to the different instruments that were used to collect the data.

The first and probably most important observation in Table I is that all listed useful yield values are relatively small, i.e., around or below $\sim 10^{-5}$ detected molecular ions per molecule equivalent of removed material. Comparing this finding with the ionization efficiency values given in Sec. IV A, it is immediately evident that there must be other factors limiting the observed molecular useful yield besides the poor ionization efficiency. Using the estimate of $\alpha_M^+ \geq 10^{-3}$ for molecules sputtered under C₆₀ bombardment as given in Sec. IV A, it is clear that useful yields that are currently measured under C₆₀ bombardment can only be improved up to values of the order of 10⁻² or below via enhancement of the ionization efficiency. It is seen from Table I that the different attempts to utilize projectile induced chemistry are successful to an extent that they can boost the protonation efficiency of a sputtered trehalose molecule up by about 2 orders of magnitude as compared with C₆₀ and bare rare gas cluster ion beams. Assuming similar “intrinsic” ionization probabilities as measured for guanine and coronene for trehalose as well, there seems to be headroom for one or 2 more orders of magnitude improvement. This finding is encouraging, and more effort is obviously needed in order to optimize the efficiency of the chemical ionization process for sensitivity enhancement.

On the other hand, it is obvious that the low useful yield observed in molecular SIMS cannot be only due to poor ionization. The data presented here indicate a discrepancy by 2 orders of magnitude or more between hypothetical useful secondary ion yields that could be obtained with unit ionization efficiency and actually measured SIMS data. Part of this discrepancy is certainly caused by the instrumental collection and detection efficiency, leading to *T* values below unity in Eq. (4). Particularly the difference between the values reported for C₆₀ bombardment under the same impact conditions must clearly be caused by such effects. The remaining limitation must

TABLE I. Useful molecular ion yield determined for (quasi-)molecular ions sputtered from a trehalose film under bombardment with different cluster ion beams. The data have been calculated from published or unpublished work (see references besides the ion symbol), for details of the calculation see text. The symbol besides the kinetic impact energy denotes the instrument type on which the data were taken.

	Bi ₃ (Ref. 51) 30 keV ^a	Au ₃ (Ref. 47) 25 keV ^b	C ₆₀ (Ref. 47) 20 keV ^b	C ₆₀ (Ref. 48) 40 keV ^b	C ₆₀ (Refs. 52 and 53) 40 keV ^c	Ar _n (Refs. 37 and 52) 20 keV ^c	Ar _n + HCl (Ref. 37) 20 keV ^c	(H ₂ O) _n (Ref. 42) 20 keV ^c
[M-OH] ⁺	4×10^{-6}	1×10^{-6}	5×10^{-6}	2×10^{-5}	2×10^{-6}	2×10^{-6}	2×10^{-6}	6×10^{-6}
[M+H] ⁺	2×10^{-7}		2×10^{-6}		5×10^{-8}	8×10^{-8}	2×10^{-6}	6×10^{-6}
[M-H] ⁻					8×10^{-7}	4×10^{-6}	3×10^{-8}	
[M+Na] ⁺			7×10^{-6}	4×10^{-5d}	1×10^{-6}	5×10^{-6d}	2×10^{-6}	4×10^{-8}
[M+Cl] ⁻						1×10^{-6d}	9×10^{-7}	

^aTOF-SIMS V.

^bBioToF.

^cJ105 (PSU).

^dSalt saturated, otherwise by factor 5 (Na) and 200 (Cl) lower [see Fig. 6 and Lu *et al.* (Ref. 48)].

then be attributed to collision induced fragmentation, i.e., the breakup of a parent molecule during its emission from the surface. In that context, it should be noted that it is not easy to determine the survival probability entering Eq. (4) from measured SIMS or SNMS spectra, since (1) all fragments may in principle exhibit different (post-) ionization efficiency and (2) one single fragmentation of the parent molecule might lead to multiple product ions in the following fragmentation chain. Assuming the same ionization efficiency for all detected fragments, one can make a crude estimate of p_{surv} by relating the molecular ion signal to the total fragment ion signal observed in the measured SIMS spectra at all masses below the molecular ion mass. For trehalose, the respective value can be determined from the data presented in Fig. 5. Counting the sum of $[M+H]^+$ and $[M+Na]^+$ signals to be representative for the intact molecule, one finds survival probabilities of 0.06 under 40 keV C_{60}^+ and 0.28 under 20 keV Ar_{2000}^+ bombardment, respectively. Including the $[M-OH]^+$ fragments into the quasi-molecular ion signal, these values increase to 0.15 (C_{60}) and 0.40 (Ar_{2000}), respectively. The true values of p_{surv} may still be lower, since fragment ions at $m/z < 100$ are not efficiently detected in the J105 instrument used to acquire the data of Fig. 5.

Although being obtained under rather crude assumptions regarding the ionization efficiency of the fragments, these data indicate that collision induced fragmentation of the sputtered molecules may indeed reduce the useful yield by more than 1 order of magnitude, with 40 keV C_{60} acting worse than 20 keV Ar_{2000} . It should be noted at this point that many more low mass fragments are generally observed in the spectra of postionized sputtered neutrals. Here, however, it is not easy to distinguish between signals arising from postionization of neutral fragments produced in the sputtering process (which represent the signals that would be of interest for the determination of p_{surv}) and those generated by the postionization process itself via photofragmentation of intact neutral molecules, so that an evaluation of the collisional fragmentation probability from measured postionization spectra appears difficult.

V. CONCLUSIONS

The relatively low molecular useful yield, which is generally observed in cluster-SIMS experiments is often attributed to the poor ionization efficiency of the molecules desorbed from the surface. This notion can now be examined in more detail due to the fact that quantitative experimental data on the ionization probability of some sputtered molecules have recently become available. The measurements performed for coronene or guanine molecules indicate that the currently achieved intrinsic ionization efficiency obtained under bombardment with C_{60} or Ar_n cluster ion beams is better than 1 %, leaving headroom of about 2 orders of magnitude for improvement of the detection sensitivity of (quasi-)molecular secondary ions via enhancement of the ionization efficiency.

Among the possible strategies for such an enhancement, the use of high energy projectile ions—which has been advocated under the name “MeV-SIMS” as a tool for efficient

molecular ion detection—is shown to improve the (physical?) ionization mechanism of coronene molecules, albeit with only a moderate enhancement of the order of a factor two. Regarding chemical ionization, the data compiled here for the trehalose model system indicate that the ionization efficiency can be significantly enhanced via projectile induced surface chemistry if suitable chemically reactive projectile clusters are being used. Under optimized conditions, the protonation efficiency of a sputtered intact trehalose molecule can be enhanced by about 2 orders of magnitude over that observed under C_{60} bombardment, as expected from the measured ionization probability values obtained for these projectiles. At the same time, the (de)protonation efficiency becomes comparable to the (an-)cat-ionization efficiency obtainable via salt addition. At least for the trehalose system discussed here, these findings indicate that there might be a saturation limit for chemical ionization efficiency enhancement. Combining the measured intrinsic ionization probability with the currently observed enhancement, one would conclude that the ionization efficiency of a sputtered intact molecule can now be boosted up to the ~10% level, indicating that there not might be much more to be gained in sensitivity by continued efforts to tune the chemistry in the impact zone. In any case, the compiled useful yield data shows that poor ionization efficiency cannot be the only factor limiting molecular detection sensitivity in cluster SIMS, thereby calling for further strategies to reduce the collision induced fragmentation.

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¹N. Winograd, *Anal. Chem.* **77**, 142A (2005).

²*Cluster Secondary Ion Mass Spectrometry: Principles and Applications*, edited by C. M. Mahoney (Wiley, Hoboken, NJ, 2013).

³J. C. Vickerman and N. Winograd, *Int. J. Mass Spectrom.* **377**, 568 (2015).

⁴J. Vickerman and N. Winograd, *Cluster Secondary Ion Mass Spectrometry* (Wiley, Hoboken, 2013), pp. 269–312.

⁵J. S. Fletcher, N. P. Lockyer, and J. C. Vickerman, *Mass Spectrom. Rev.* **30**, 142 (2011).

⁶C. M. Mahoney, *Mass Spectrom. Rev.* **29**, 247 (2010).

⁷J. S. Fletcher and J. C. Vickerman, *Anal. Bioanal. Chem.* **396**, 85 (2010).

⁸S. Sheraz, A. Barber, I. B. Razo, J. S. Fletcher, N. P. Lockyer, and J. C. Vickerman, *Surf. Interface Anal.* **46**, 51 (2014).

⁹S. M. Hankin, D. M. Villeneuve, P. B. Corkum, and D. M. Rayner, *Phys. Rev. A* **64**, 013405 (2001).

- ¹⁰A. Wucher, in *TOF-SIMS: Materials Analysis by Mass Spectrometry*, edited by J. C. Vickerman and D. Briggs (IM Publications/Surface Spectra, Chichester, 2013), pp. 217–246.
- ¹¹N. J. Popczun, L. Breuer, A. Wucher, and N. Winograd, *J. Am. Soc. Mass Spectrom.* **28**, 1182 (2017).
- ¹²N. J. Popczun, L. Breuer, A. Wucher, and N. Winograd, *J. Phys. Chem. C* **121**, 8931 (2017).
- ¹³L. Breuer, A. Kucher, M. Herder, A. Wucher, and N. Winograd, *J. Phys. Chem. A* **118**, 8542 (2014).
- ¹⁴A. Kucher, A. Wucher, and N. Winograd, *J. Phys. Chem. C* **118**, 25534 (2014).
- ¹⁵P. Williams, *Appl. Surf. Sci.* **13**, 241 (1982).
- ¹⁶Z. Sroubek, *Spectrochim. Acta, Part B* **44**, 317 (1989).
- ¹⁷M. L. Yu, *Sputtering by Particle Bombardment III*, edited by R. Behrisch and K. Wittmaack (Springer, Berlin, 1991), Vol. III, pp. 91–160.
- ¹⁸K. Wittmaack, *Mat.-Fys. Medd.-Kgl. Dan. Vidensk. Selsk.* **52**, 465 (2006).
- ¹⁹A. Wucher, *Appl. Surf. Sci.* **255**, 1194 (2008).
- ²⁰K. Wittmaack, *Surf. Sci. Rep.* **68**, 108 (2013).
- ²¹K. Wittmaack, *Anal. Chem.* **86**, 5962 (2014).
- ²²B. Hagenhoff, *TOF-SIMS: Materials Analysis by Mass Spectrometry*, edited by J. C. Vickerman and D. Briggs (Surface Spectra Ltd., Chichester, 2013), pp. 193–216.
- ²³A. Wucher, W. Berthold, and H. Oechsner, “The charge state of sputtered metal clusters,” in *Secondary Ion Mass Spectrometry (SIMS IX)*, edited by A. Benninghoven, Y. Nihei, R. Shimizu, and H. W. Werner (Wiley & Sons, Yokohama, 1993), pp. 100–103.
- ²⁴M. Wahl and A. Wucher, *Nucl. Instrum. Methods, B* **94**, 36 (1994).
- ²⁵R. Heinrich and A. Wucher, *Nucl. Instrum. Methods, B* **140**, 27 (1998).
- ²⁶R. Heinrich, C. Staudt, M. Wahl, and A. Wucher, “Ionization probability of sputtered clusters,” in *Secondary Ion Mass Spectrometry (SIMS XII)*, edited by A. Benninghoven, P. Bertrand, H.-N. Migeon, and H. W. Werner (Elsevier, Amsterdam, 2000) pp. 111–114.
- ²⁷C. Staudt, R. Heinrich, and A. Wucher, *Nucl. Instrum. Methods, B* **164–165**, 677 (2000).
- ²⁸C. Staudt and A. Wucher, *Phys. Rev. B* **66**, 075419 (2002).
- ²⁹S. Ghalab *et al.*, *Nucl. Instrum. Methods, B* **197**, 43 (2002).
- ³⁰S. Meyer, C. Staudt, and A. Wucher, *Appl. Surf. Sci.* **203–204**, 48 (2003).
- ³¹A. Samartsev and A. Wucher, *Appl. Surf. Sci.* **252**, 6474 (2006).
- ³²A. Samartsev, “Sputtering of indium under polyatomic gold cluster bombardment,” Ph.D. thesis (Universität Duisburg-Essen, 2006).
- ³³A. Wucher, *Izv. Akad. Nauk. Ser. Fiz.* **66**, 499 (2002).
- ³⁴M. Herder, J. Klein, and A. Wucher, “Ionization of coronene sputtered under 20-keV C₆₀⁺ impact,” Universität Duisburg-Essen, 2017 (unpublished).
- ³⁵L. Breuer *et al.*, “Secondary neutral mass spectrometry with MeV and keV projectiles,” paper presented at the Secondary Ion Mass Spectrometry (SIMS XXI conference, Krakow, 2017).
- ³⁶A. Wucher, H. Tian, and N. Winograd, *Rapid Commun. Mass Spectrom.* **28**, 396 (2014).
- ³⁷H. Tian, A. Wucher, and N. Winograd, *J. Am. Soc. Mass Spectrom.* **27**, 285 (2016).
- ³⁸H. Tian, D. Maciazek, Z. Postawa, B. J. Garrison, and N. Winograd, *J. Am. Soc. Mass Spectrom.* **27**, 1476 (2016).
- ³⁹K. Moritani *et al.*, data presented at the Secondary Ion Mass Spectrometry (SIMS-XXI) Conference, Krakow, 2017.
- ⁴⁰S. Sheraz, A. Barber, J. S. Fletcher, N. P. Lockyer, and J. C. Vickerman, *Anal. Chem.* **85**, 5654 (2013).
- ⁴¹I. B. Razo, S. Sheraz, A. Henderson, N. P. Lockyer, and J. C. Vickerman, *Surf. Interface Anal.* **46**, 136 (2014).
- ⁴²S. S. N. Rabbani, I. B. Razo, T. Kohn, N. P. Lockyer, and J. C. Vickerman, *Anal. Chem.* **87**, 2367 (2015).
- ⁴³I. Berrueta Razo, S. Sheraz, A. Henderson, N. P. Lockyer, and J. C. Vickerman, *Rapid Commun. Mass Spectrom.* **29**, 1851 (2015).
- ⁴⁴A. Delcorte and P. Bertrand, *Appl. Surf. Sci.* **231–232**, 250 (2004).
- ⁴⁵A. Heile *et al.*, *Appl. Surf. Sci.* **255**, 941 (2008).
- ⁴⁶A. Delcorte and P. Bertrand, *Anal. Chem.* **77**, 2107 (2005).
- ⁴⁷J. Cheng, A. Wucher, and N. Winograd, *J. Phys. Chem. B* **110**, 8329 (2006).
- ⁴⁸C. Lu, A. Wucher, and N. Winograd, *Surf. Interface Anal.* **43**, 99 (2011).
- ⁴⁹A. Wucher, “Transmission and detection efficiency in a J105 Chemical Imager,” The Pennsylvania State University, 2015 (unpublished).
- ⁵⁰M. P. Seah, *J. Phys. Chem. C* **117**, 12622 (2013).
- ⁵¹C. Heuser and A. Wucher, “Analysis of trehalose films performed in a ToF-SIMS V instrument,” Universität Duisburg-Essen, 2015 (unpublished).
- ⁵²H. Tian, “Analysis of trehalose films using a J105 Chemical Imager,” The Pennsylvania State University, 2017 (unpublished).
- ⁵³K. Shen, A. Wucher, and N. Winograd, *J. Phys. Chem. C* **119**, 15316 (2015).