Chemical Bonding

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Oscillations in the Stability of Consecutive Chemical Bonds Revealed by Ion-Induced Desorption**

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Abstract: *While it is a common concept in chemistry that strengthening of one bond results in weakening of the adjacent ones, no results have been published on if and how this effect protrudes further into the molecular backbone. By binding molecules to a surface in the form of a self-assembled monolayer, the strength of a primary bond can be selectively altered. Herein, we report that by using secondary-ion mass spectrometry, we are able to detect for the first time positional oscillations in the stability of consecutive bonds along the adsorbed molecule, with the amplitudes diminishing with increasing distance from the molecule–metal interface. To explain these observations, we have performed molecular dynamics simulations and DFT calculations. These show that the oscillation effects in chemical-bond stability have a very general nature and break the translational symmetry in molecules.*

Self-assembled monolayers (SAMs)[1] are a nanotechnological system, in which molecules are chemically bonded to a substrate in an ordered and oriented fashion. The influence of the strength of the molecule-substrate bond on the structure and stability of SAMs is still poorly understood even for the most simple system of methanethiol on Au(111).[2] As it is known from other fields of chemistry, the formation of a strong bond (in this case to the surface) should lead to a weakening of the adjacent bonds within the molecules. Thus, it would be interesting from a very basic point of view as well as technologically relevant to determine these influences.

We decided to take a new approach by exploiting static secondary-ion mass spectrometry (SSIMS) in combination with the molecular dynamics (MD) simulation of such experiments and density functional theory (DFT) calculations. As model SAMs we have selected two homologous series of the general form CH_3-$(C_6H_4)_2$-$(CH_2)_n$-S(Se)/Au(111), (BP*n*S(Se), $n = 1$–6), for which either sulfur atoms or selenium atoms (BP*n*Se) act as a binding groups to the Au(111) substrate. Previous microscopic[3–5] and spectroscopic[6–9] studies demonstrated that the BP*n*S(Se)/Au(111) packing structure, unlike other SAMs, remains virtually the same for the S and Se analogues within both series. This means that intermolecular interactions in these SAMs are identical when comparing the respective members of both families and thus the only source of difference in stability between them is the binding atom (S vs. Se). Analysis of such SAMs gives a direct way to trace molecule–substrate interface energetics.

Positive and negative SSIMS mass spectra are presented in Figure S1 in the Supporting Information. The most interesting information is found in the positive mass spectra where a significant emission of secondary ions related to the complete molecule $M_{S/Se}^+$ and its desulfurized ($[M{-}S]^+$) or deselenized ($[M{-}Se]^+$) fragments, respectively, is observed. Interestingly, the M_S^+ emission is much higher than the M_{Se}^+, while the emission of $[M{-}S]^+$ is much lower than the that of $[M{-}Se]^+$ (see Figure S2). Since emission of an $M_{S/Se}^+$ ion requires Au–S(Se) bond scission, we can correlate a stronger M_S^+ signal with a lower stability of the Au–S bond compared to the Au–Se bond, in line with previous exchange experiments.[10] Following this argumentation, we can correlate the reduced emission of $[M{-}S]^+$ compared to $[M{-}Se]^+$ with a higher stability of the S–C bond than the Se–C bond in these SAMs. Such behavior could be explained considering that the valence electrons of the S (or Se) atom are involved in bonding with the Au substrate atom and with its neighboring C atom. The increased involvement of valence electrons of the S(Se) atom in one of these chemical bonds should result in lower involvement of these electrons in the second bond, consequently reducing the stability of the second bond. We may ask if modifying the strength of the bond to the substrate by an S→Se substitution will influence additional chemical bonds in its vicinity. To answer this question, we have calculated the intensity ratio of the signals of identical ions ejected from BP*n*S/Au(111) and BP*n*Se/Au(111) SAMs ($n =$ 2–4). These ions were generated by the scission of one of four consecutive chemical bonds along the molecular chain, starting from the headgroup atom (Figure 1 a). The resulting data (Figures 1 b–d) show a very clear positional oscillation which decreases with increasing distance from the metal–molecule interface. Following previous argumentation the substitution of the S atom by the more strongly bound Se

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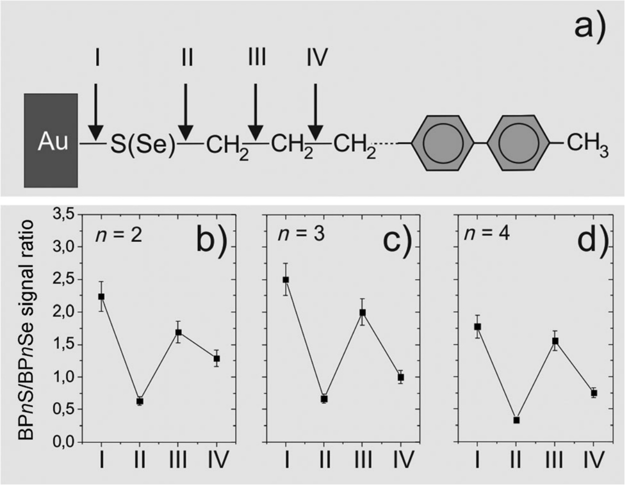

Figure 1. SSIMS data analysis. a) the location of the four probed, consecutive chemical bonds. Emission of M^+, $[M{-}S(Se)]^+$, $[M{-}CH_2S(Se)]^+$, and $[M{-}CH_2CH_2S(Se)]^+$ secondary ions corresponds to scission of bond I, II, III, and IV, respectively. b–d) the relative intensities of the positive ions emitted from BPnS/Au(111) and BPnSe/Au(111) SAMs (for $n=2$ (b), $n=3$ (c) and $n=4$ (d)) corresponding to the scission of indicated bonds.

atom leads to a shift of valence electrons from the neighboring Se–C^1 bond towards the Au–Se bond reducing the stability of the Se–C^1 bond. The decrease in the Se–C^1 bond stability results, in turn, in a shift of the valence electrons of the C^1 atom towards the C^2 atom leading to an increased strength of the C^1–C^2 bond, and so on. As a consequence, we propose that: 1) increase of stability of the headgroup atom bonding to the substrate by changing from S→Se induces a chain of alternating modifications of the stability of the neighboring chemical bonds in the molecule, and 2) the disturbances introduced into electronic structure of the aliphatic chain by chemical bonding to the substrate by the headgroup atom diminish at larger distances from the molecule–substrate interface because the dislocation of the valence electrons becomes less and less.

Our analysis indicates an alternating change of the bond stability on comparison of the respective data from the thiol and selenol series. We may ask if a similar effect can be observed within each of these homologous series separately and how these changes are related to each other? As shown in Figure 2a–c a significant odd–even variation (with respect to the number n within each series) exists for the emission of $[C_{15}H_{15}]^+$, $[C_{14}H_{13}]^+$, and $[C_{16}H_{17}]^+$ fragments from the BPnS(Se)/Au(111) SAMs. To desorb for instance a $[C_{15}H_{15}]^+$ fragment from BPnS(Se)/Au(111) SAMs with an increasing number n along the homologous series, consecutive chemical bonds have to be cleaved (Figure 2a). Thus, for $n=1$ the S(Se)–C^1 bond has to be cleaved, for $n=2$ the C^1–C^2 bond, and so on. The data shown in Figure 2a deliver several crucial pieces of information. First, considering our proposition that the relative signal of identical ions ejected from BPnS/Au(111) and BPnSe/Au(111) SAMs is proportional to the strength of the bond that needs to be broken, the odd–even oscillation in Figure 2a indicates alternating changes in the

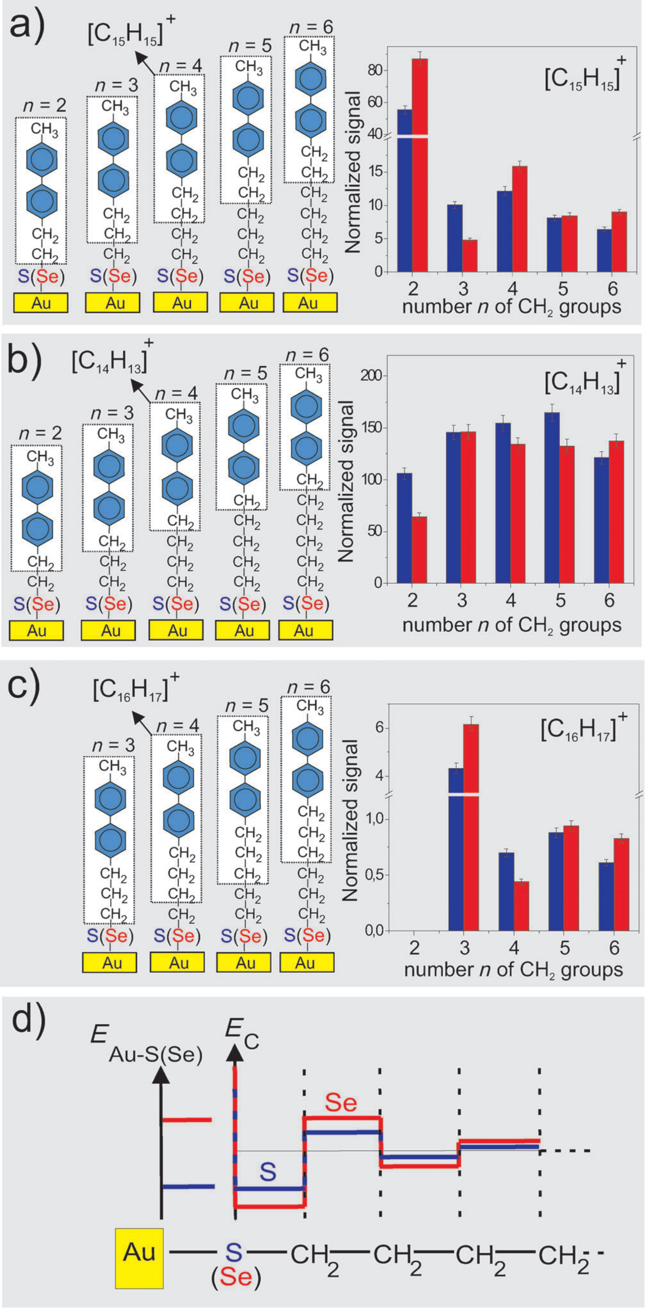

Figure 2. SSIMS data analysis. a) the normalized signal of the $[C_{15}H_{15}]^+$ emission for BPnS/Au(111) (blue bars) and BPnSe/Au(111) (red bars). b) the respective data for the $[C_{14}H_{13}]^+$ emission and c) for the $[C_{18}H_{17}]^+$ emission. The white boxes in the schemes on the left side of panels (a)–(c) show which part of the individual molecules corresponds to the given type of secondary ion, also indicating the location of the scission resulting in its emission. Note that the phase of this odd–even effect depends on the length of the analyzed fragment and, therefore, this odd–even effect is not a consequence of the established odd–even[2,3] variation in the film density of these SAMs. d) Summary of the SSIMS results: i) The higher bond energy of Se–Au than S–Au and ii) the resulting oscillations in the bond energies of the consecutive bonds along the molecular backbone. The effect diminishes with increasing distance from the molecule–substrate interface, but generally shows a higher amplitude for the selenium-based SAMs.

stability of consecutive chemical bonds along the molecule in the direction away from the molecule–substrate interface towards the biphenyl group. Second, this bond-stability oscillation effect has the same phase for BP*n*S/Au(111) and BP*n*Se/Au(111) SAMs with, however, much higher modulation amplitude for the Se system. Third, the amplitude of these oscillations quickly diminishes with increasing distance from the molecule–substrate interface. All these observations are fully consistent with the data shown in Figure 1. Following our simple qualitative explanation, more pronounced oscillations are expected for BP*n*Se/Au(111) as compared to BP*n*S/Au(111) SAMs owing to a stronger bonding of the Se system to the Au(111) substrate. These conclusions are supported by analogous data shown in Figure 2b, where the strong signal of the $[C_{14}H_{13}]^+$ fragment is analyzed. This fragment is shorter by one CH_2 group than the $[C_{15}H_{15}]^+$ fragment therefore we need to shift our analysis by one chemical bond away from the molecule–substrate interface. As a result, the amplitude of the oscillations is reduced because of the greater distance from the molecule–substrate interface and, more importantly, the phase of the odd–even effect is reversed. A similar trend is also present in the somewhat weaker signal of the $[C_{16}H_{17}]^+$ fragment which can only be emitted for $n = 3$–6. In this case, we need to shift the analysis by one chemical bond in the direction of the molecule–substrate interface as compared to the analysis for the $[C_{15}H_{15}]^+$ fragment. As expected, data shown in Figure 2c fully confirm such a scenario for both BP*n*S/Au(111) and BP*n*Se/Au(111) SAMs: a stronger odd–even effect and a reversal of the phase can be observed. Again, the magnitude of the odd–even oscillation is higher for the BP*n*Se/Au(111) SAMs and diminishes in both cases with increasing number *n*. Note that the phase of this odd–even effect depends on the length of the analyzed fragment and, therefore, this odd–even effect is *not* a consequence of the known odd–even[2,3] variation in the film density of these SAMs.

We believe that the above SSIMS measurements reveal for the first time the oscillation of bond stability along the molecule backbone as shown schematically in Figure 2d. It is worth mentioning that such a modulation of bond energy cannot only be attained by changing the anchoring atom (S→Se), but also the substrate (Au→Ag), which results in very similar observations (data will be published elsewhere). However, in all cases our hypothesis postulates that the emission efficiency of a given molecular secondary ion is correlated with the stability of the respective chemical bond that has to be cleaved to enable emission of this ion. The justification of such a correlation is discussed in detail in the Supporting Information. In short, two issues must be considered: the desorption and the ionization mechanism. Two distinct desorption mechanisms leading to the emission of neutral molecular fragments were identified by previous studies on collision-cascade and chemical-reaction based processes.[11–14] Whereas the chemical reaction mechanism quite naturally explains the high sensitivity of emission towards the stability of the respective cleaved bond, such sensitivity for the energetic collision-cascade based emission is not obvious. To address this issue we have performed simulations of BP3S/Au(111) sputtering induced by 8 keV Bi atoms using MD simulations. To probe possible influences of the Au−S and S−C bond stability on the efficiency of the sputtering process, two sets of MD simulations have been performed (Figures 3 and S3). The first set of calculations was performed on a BP3S/Au(111) system having non-modified Au−S and S−C bond strength, while the second set of simulations was performed on a system, where the Au−S bond strength was increased by 10% and the S−C bond strength was reduced by 10%. The data presented in Figure 3 show that even such a small modification of bond strengths results in a 40% reduction in $[M]^+$ emission (scission of the Au−S bond) and an almost 100% increased emission of $[M{-}S]^+$ fragments (scission of the S−C bond). These results are consistent with our SSIMS data in Figure S2 and confirm that small changes in the stability of the chemical bonds can strongly affect the collision-cascade based emission. We can, therefore, conclude that both, desorption of molecular fragments by ion-induced chemical reactions or by simple collision-cascade mechanisms, are correlated with the stability of the respective bonds, which become cleaved during the desorption process. But can this trend be altered by the ionization process? As detailed in the Supporting Information, this presumably is not the case. Generally, experiments

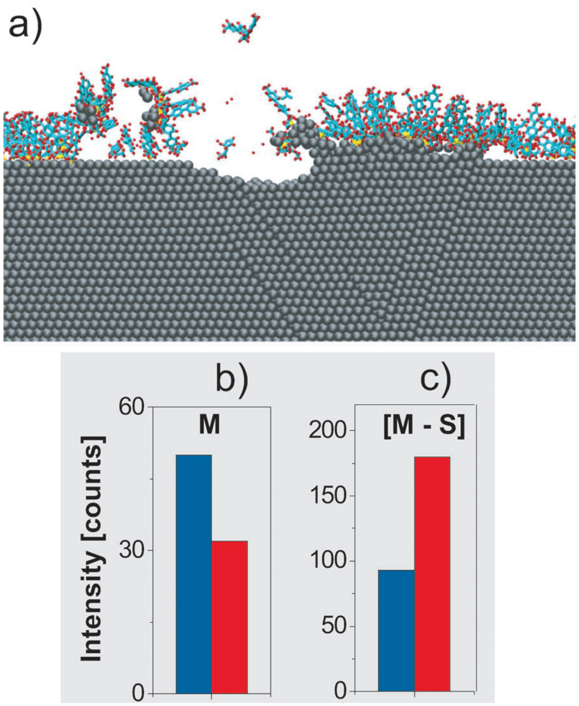

Figure 3. Analysis of MD simulations for the sputtering of BP3S/Au(111) SAMs with 8 keV Bi projectiles. a) the impact of a single Bi^+ projectile on a BP3S/Au(111) SAM. b),c) the emission of the complete molecule (*M*) and desulfurized fragment (*M*−S) resulting from a compilation of 1100 impact events: blue bars correspond to the emission from native BP3S/Au(111) system and red bars corresponds to a modified BP3S/Au(111) system, in which the Au−S bond strength was increased by 10% and the S−C bond strength was decreased by 10%. Full mass spectra calculated for both systems are shown in Figure S3.

analyzing emission of neutral fragments[13,14] and the DFT calculations for these SAMs[15] with the possible ionization process by electron transfer[16] or by excited precursor fragmentation[16] show that the ionization process does not influence significantly the correlation between desorption process and stability of a cleaved chemical bond.

To understand if an alternating strengthening and weakening of several consecutive bonds can in fact be the result of a change at a terminal bond, we have performed DFT calculations. First, binding energies of chemical bonds within an individual BP3S molecule adsorbed on the Au(111) surface were analyzed. The results are shown in Figure 4a exhibiting clear oscillation in the binding energy of consecutive chemical bonds. Comparing the phase of the observed oscillations with the SSIMS experiments shown in Figure 2, we conclude that a higher emission of a given secondary ion is indeed correlated with a lower binding energy of the respective chemical bond that has to be cleaved. As a next step, calculations for unbound BP3SH and BP3SeH molecules were performed (Figure 4b,c) exhibiting an oscillation in the binding energy of consecutive bonds with the same phase as for the Au(111) surface bonded molecule. Moreover the amplitude of these oscillations is clearly higher for the Se based molecule. To separate the influence of the biphenyl group on the observed oscillations, the bond strengths in long alkanethiol and alkaneselenol molecules were calculated (Figure 4d,e). These data show a quickly diminishing oscillation in binding energies with increasing distance from the SH/SeH terminus, again with higher amplitude for the SeH case. Altogether, these calculations clearly indicate that the observed effect of the bond stability oscillation is not exclusively related to the molecule–substrate interface but has a much more general character in chemistry. In this case, the substitution of a methylene group (C−C bond energy 3.55 eV) by a sulfur or selenium atom (C−S and C−Se bond energy 2.92 and 2.58 eV, respectively) results in breaking the translational symmetry in the aliphatic chain by modifying the energy of the next three consecutive C−C bonds with a decreasing oscillating strength, finally recovering the 'normal' value of 3.55 eV. For BP3SH molecules this effect is significantly amplified since the other end of the short aliphatic chain is attached to a biphenyl group with a much stronger C^3–C^4 bond (4.1 eV) which itself causes similar oscillations amplifying this effect in comparison to long alkanethiols.

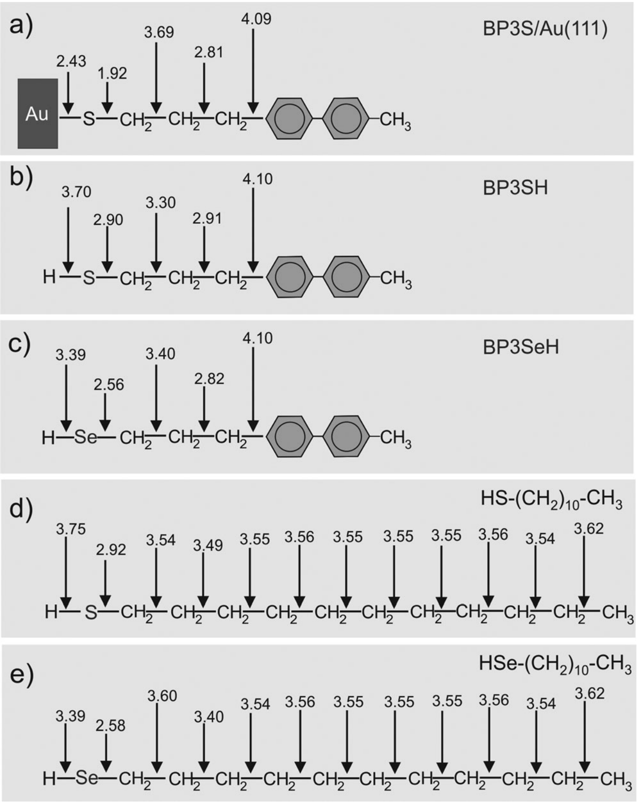

Figure 4. Summary of the DFT calculation results for individual bond energies (in [eV]) for a) the BP3S/Au(111) monolayer, b) free BP3SH molecule, c) free BP3SeH molecule, d) free HS-$(CH_2)_{10}$-CH_3 molecule, and e) free HSe-$(CH_2)_{10}$-CH_3 molecule.

In conclusion, our experiments and calculations show that by using the SSIMS technique we can not only trace the changes in the binding stability of SAMs, but, more importantly, analyze subtle variations in the molecule's internal energetics. With this approach, we could find positional oscillations in bond energy, that are not only related to the molecule–substrate interface, but have a general character in chemistry related to breaking translational symmetry in molecules. Although chemically quite intuitive, it is very surprising that this effect has neither been described nor considered before in the literature. It is reasonable to assume that these effects became blurred in the more traditional techniques, such as thermal or electrochemical desorption, owing to the comparably slow ramping of the global energies (temperature or potential, respectively). This slow ramping permits a reconstruction of molecule–substrate interface which affects the bond-cleavage processes. To detect the effect of the binding energies directly, the exploitation of the pico-second time scale of the desorption processes within the SSIMS technique was essential.

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