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Charge Delocalization Induces Reaction in Molecular Chains at a Surface**

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The scanning tunneling microscope (STM) enables studies of electron-induced reaction at the molecular scale. The STM tip is used to deliver an electron to a single adsorbed molecule, after which the reaction products at the surface are observed. Pioneering experimental work has been performed at semiconductor[1–3] and metal surfaces.[4–10] Non-adiabatic ionic excitation plays a major role for electron-induced reactions occurring at surfaces. Molecules remain in the excited ionic potential energy surface, designated pes* over a sufficient period of time for acceleration and distortion prior to reversion to the ground potential energy surface (pes).[11]

Maksymovych, Yates and co-workers have made a detailed experimental study of the electron-induced reaction of isolated dimethyldisulfide (CH_3SSCH_3) molecules physisorbed at single-crystal gold surface.[12,13] The *trans* (rather than *cis*) conformation of the parent molecule was retained, after S–S bond-rupture, in the two chemisorbed products, thiyls (CH_3S). The product thiyls were bound to the surface predominantly two lattice spacings (5.5 Å) apart. In subsequent work Maksymovych et al.[14,15] extended their study of this electron-induced reaction to self-assembled linear chains of dimethyldisulfide molecules. They obtained the striking result that, following a single electron-pulse with the tip of the STM placed over a selected molecule either at the end or in the middle of a line of physisorbed molecules, numerous adjacent S–S bonds broke to form new S–S bonds to neighboring physisorbed dimethyldisulfide molecules. This exchange reaction propagated along lines of up to 10 neighboring dimethyldisulfide molecules. They proposed that this might be a consequence of a chain reaction, propagated in one or both directions along the chain by recoiling "hot" thiyl radicals.

Since they did not model the dynamics, we have done so for the first time herein. We make use of an "impulsive two-state" model that we have employed in earlier experimental plus theoretical studies of the dynamics of the electron-induced reaction of paradiiodobenzene[16] and paradichlorobenzene[17] at Cu(110). Herein, to shed light on the cited experimental work, we model dimethyldisulfide physisorbed on Au(111). Our model makes use of molecular dynamics (MD) implemented in Vienna Ab-initio Simulation Package (VASP).[18] This approach is at first applied to dimethyldisulfide on an approximation to the DFT repulsive anionic excited potential-energy surface (pes*; see Supporting Information, Section 1.2). This is followed, after a minimum residence time, t^*, required for subsequent reaction on the DFT ground pes, by MD on the ground pes as the molecule forms differently bound physisorbed reaction products and also a pair of thiyl chemisorbed reaction products, as in the experimental studies by Maksymovych, Yates, and co-workers[12,13] described above. The brief time, t^* on pes* provides the initial impulse for this complex reaction to occur. The major forces are, however, released in the much longer time spent by the system on the ground pes en route to products. This impulsive two-state model, described in our previous work,[16,17,19] is denoted as I2S. It is extended herein to encompass multiple impulses arising from delocalized charge, occurring concurrently in a "distributed impulsive two-state" model (D-I2S).

For the case of a single dimethyldisulfide molecule we shall show that the I2S model gives dynamics in full accord with that postulated by Maksymovych, Yates, and co-workers on the basis of their observed STM images. For pairs of dimethyldisulfide the I2S model predicts that the recoiling thiyl radicals, even in their most-energized condition, rebound from the neighboring molecules without reaction, ruling out the radical-induced chain reaction suggested by Maksymovych, Yates, and co-workers. Instead we propose herein, and examine for lines of up to four dimethyldisulfide molecules on Au(111), a novel mechanism based on the delocalization of the added charge giving rise to simultaneous impulses distributed along the entire length of the chain; the model termed D-I2S.

According to this new model, D-I2S, during the entire time t^* that the linear assembly spends on the anionic pes* the partial charge that resides in the antibonding orbitals of all the molecules in the line (the "distributed impulse") stretches all of their S–S bonds slightly (by ca. 0.3 Å). On transfer to the ground pes this multiple stretch along the reaction coordinate (along with other lesser distortions in the anionic molecule) is sufficient to initiate S–S bond breaking in the reagent dimethyldisulfide molecules, and the formation of new S–S

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bonds to the neighboring dimethyldisulfide molecules in an exothermic reaction that yields differently aligned physisorbed dimethyldisulfide as well as giving rise to two chemisorbed thiyls. The postulated delocalization of charge when combined with the molecular dynamics embodied in the distributed I2S model accounts, therefore, qualitatively for the remarkable observation of Maksymovych, Yates et al. that added charge, at whatever point in the chain it is introduced, can result in the 'collective reactivity of molecular chains'. Our model, in order to provide a sufficient repulsive impulse to all the existing S−S bonds so as to form new S−S bonds, requires only a single added electron for a two-member chain, but two added electrons for the facile reaction of three- and four-member chains. The cited experiments do not give a conclusive statement as to whether, and for what chain-lengths, single or double electronic excitation is required.

In what follows we apply our distributed model, D-I2S, in turn, to the electron-induced reaction of single dimethyldisulfide molecules, followed by the reaction of linear assemblies of dimers, trimers, and tetramers of dimethyldisulfide. For a single molecule the delocalization of charge is over the two S-atoms. For dimers, trimers, and tetramers the delocalization is over 4, 6, and 8 S-atoms, respectively.

Figure 1, adapted from Maksymovych, Yates et al.,[14] reproduces their molecular model of the reactive change in conformation, which they based on their STM images. The initial-state S−S bonds in Figure 1 are shown tilted upward to the right prior to reaction, and tilted upwards to the left after reaction.[20]

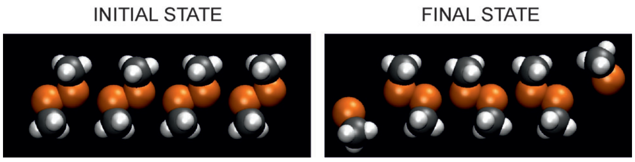

Figure 1. A dimethyldisulfide, CH_3SSCH_3, chain in a *trans* configuration on Au(111) surface, adapted from Ref. [14] (C gray, H white, S gold). The left panel is the initial state before the electron-induced reaction. The right panel is the conformation of the final state after electron-induced reaction at a surface bias of 1.2 V.

Maksymovych, Yates, and co-workers suggested that the dissociative attachment reaction of the first molecule in the chain resulted in the formation of thiyl, CH_3S, fragments with sufficient excess energy to act as chain carriers. This step required that the "hot" thiyl collided with a neighboring CH_3SSCH_3 molecule, cleaving its S−S bond and ejecting a further energized thiyl that carried on the chain reaction through successive collisions.

Herein we use our I2S model together with MD to put this hypothetical scenario to the test. Though the dissociative attachment does indeed form excited CH_3S, this fails to propagate the chain by even one molecule. Instead we propose, and demonstrate for chains of up to four CH_3SSCH_3 molecules, that a new electron-delocalization model is in good qualitative accord with Maksymovych, Yates et al.'s findings. According to this D-I2S model, the ionic charge dropped on the molecular chain immediately redistributes along the chain, applying a concurrent impulse to each of the S−S bonds in the chain. During the residence in the delocalized anionic state, the CH_3SSCH_3 molecules in the chain are energized and distorted to the extent that, when returned to the ground pes, all the molecules react on the ground pes. Reaction is found to occur by the severing of the old S−S bonds and formation of new S−S adjacent, with concurrent release of two chemisorbed CH_3S radicals at either end of the chain, as observed in the cited work.[14]

To test the applicability of this D-I2S model for the canonical case of a single dimethyldisulfide, molecule physisorbed on Au(111), starting from the optimized initial structure, an added half an electronic charge was placed on each sulfur atom by means of a pseudopotential (See Methods in Supporting Information). The minimum anionic residence time, t^* on pes* required was $t^* = 14$ fs. For $t^* < 14$ fs the system did not gain enough momentum on pes* to cross the reaction barrier on the ground pes. This minimum ionic residence time can be expected to have a higher probability than longer residence times, in light of the postulated exponential decrease in the concentration of adsorbed ions with increase in time[21] (see also Methods in Supporting Information). As shown in Figure 2 for the minimum required anionic residence ($t^* = 14$ fs) the chemisorbed thiyl reaction products retain their *trans* conformation after reaction (see "Small Impulse" Figure 2, left). Significantly, the computed separation of the S atoms in the two thiyls (5.7 Å) corresponds to the separation reported for the majority of the events studied experimentally.[12,13] The effect of increasing the residence time in the anionic state of the model to $t^* = 40$ fs is shown (Figure 2, right "Large impulse"); the thiyls have recoiled to an S···S separation of 11.6 Å corresponding to a larger separation observed in a minor pathway reported in the cited experiments, and additionally the thiyls have rotated out of their *trans* alignment as noted experimentally for this minor pathway.[13,14] For the case of electron-induced dissociation of a single dimethyldisulfide molecule on Au-

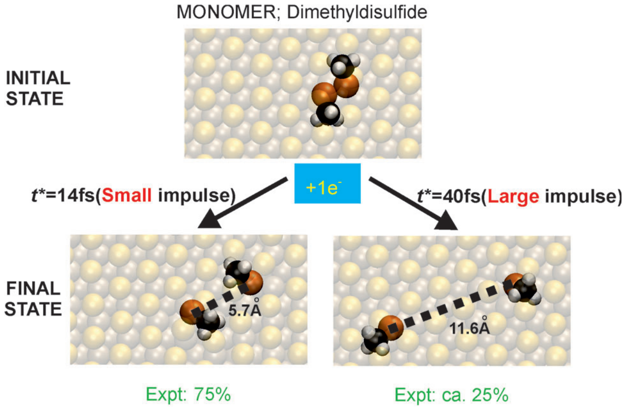

Figure 2. Application of the impulsive two-state (I2S) model to the electron-induced reaction of CH_3SSCH_3 monomer physisorbed on Au(111).

(111), the MD simulations based on the I2S model are fully consistent with the experimental findings. In what follows, therefore, we use this model to examine the earlier postulate of induced chain reaction by recoiling "hot" thiyls.

In the MD simulation pictured in Figure 3 the I2S model was used to add half an electronic charge to each S atom of the dimethyldisulfide molecule 1 (on the left in the top panel of Figure 3). This is labeled as being molecule 1 of the simplest self-assembled linear chain, namely dimeric dimethyldisulfide, with molecule 2 at the right (top panel Figure 3). The molecular dynamics calculation for electron-induced dissociation of molecule 1 gives rise to translationally and rotationally "hot" thiyl radicals which collide with molecule 2, qualitatively as postulated by Maksymovych, Yates, and coworkers. In the case of the "Small" impulse (Figure 3, left), because of the minimum anionic residence time of $t^* = 14$ fs on pes* needed for the dissociative reaction on pes, the thiyl has a translational energy of 0.31 eV. For the "Large" impulse (Figure 3, right), owing to a (less probable) $t^* = 40$ fs, this translational energy increased to 0.99 eV. In both cases, "Small" and "Large", the impacting thiyl can be seen in Figure 2 to be scattered by molecule 2 leaving the S–S bond in molecule 2 intact; that is, without radical-induced reaction.

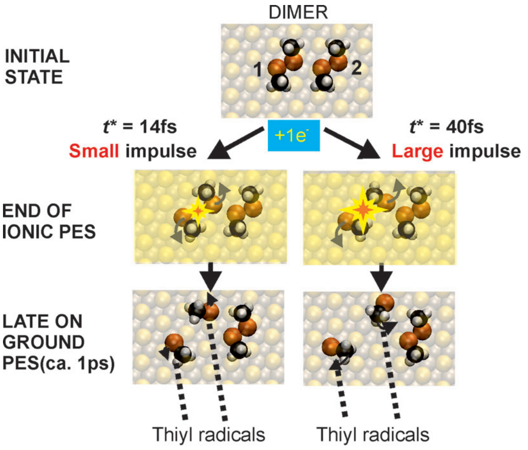

Figure 3. Molecular dynamics of single-electron-induced reaction of one physisorbed dimethyldisulfide (seen at the left) of a dimeric linear pair on Au(111). Only the molecule with the injected electron (molecule 1) reacted. For the minimum reactive ionic residence time $t^* = 14$ fs (labeled "small impulse") the recoiling and rotating thiyl radical moving to the right of dimethyldisulfide molecule 1 hit dimethyldisulfide molecule 2 at an impact parameter of 2.14 Å and bounced off. Even for a substantially longer ionic residence time, $t^* = 40$ fs (labeled "large impulse"), shown at the right, the impact of the "hot" thiyl radical recoiling from molecule 1 is seen to have failed to induce reaction in molecule 2.

As an extreme test of the viability of a radical-induced chain reaction in this system, we retained the long anionic residence time, $t^* = 40$ fs, but increased the added charge to two electrons. These electrons were both in pseudopotentials centered on the S atoms of dimethyldisulfide molecule 1. The resulting hot thiyl had a translational energy which had increased to 1.40 eV. This allowed it, on collision, to excite a minimal amount of vibration in the S–S bond of dimethyldisulfide molecule 2 (vibrational amplitude 0.05 Å), but still fell far short of inducing reaction.

The failure of the suggested radical-induced reaction, even for the simplest case of dimethyldisulfide dimer, to explain the S–S bond-rearrangement so dramatically shown in the STM experiments,[14] led us to ask whether the added charge might itself delocalize along the chain and thereby spread the site of reaction. To our knowledge charge -delocalization has not previously been proposed as the cause of reaction in physisorbed molecular chains at surfaces. Very recently Davis and co-workers[22] have shown by theory that multibond breaking should be possible in a single gaseous molecule, having non-local antibonding; they predict a remarkable four-bond breaking, but without investigation of the molecular dynamics. In the present case of molecular chains, the antibonding orbital overlap between adjacent molecules is shown in Figure 4 for the gas-phase analogue of dimethyldisulfide molecules arranged as they would be when adsorbed on Au(111). The overlap suggests that charge in these orbitals may travel along the chain. Further, we show herein by molecular dynamics that this delocalization of charge in the anionic state would sufficiently weaken the S–S bonds of the neighboring physisorbed molecules that they break in favor of the formation of new S–S bonds in the physisorbed molecular line, concurrently forming two chemisorbed thiyls, as experimentally observed. The molecular dynamics obtained by D-I2S calculations with one or two delocalized electrons added to chains of two, three, and four dimethyldisulfide molecules are reported in Figure 5. The dynamics for the most complex case of tetramer can be viewed as a movie (Supporting Information). As noted, the distribution of charge used in D-I2S was approximated (employing Gaussian 09[23]) for each of

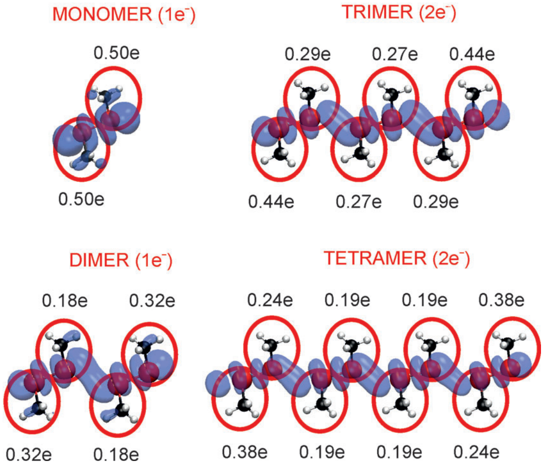

Figure 4. Pictured are the LUMOs for four gaseous molecular assemblies, corresponding in configuration to the physisorbed lines at Au(111) surfaces. The blue regions are the iso-electronic envelopes calculated by VASP using partial charge analysis. The Mulliken charge on each atom, calculated by Gaussian 09 (see Methods Section in the Supporting Information), was summed within each circle, within which S is red, C is black, and H is white. The total charges, which reside predominantly on S, are given beside the circles. This distribution of total charges was used to distribute the 1 e^- or 2 e^- in the D-I2S model.

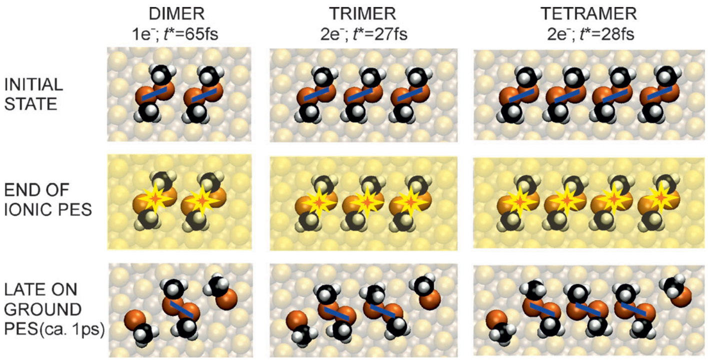

Figure 5. Molecular dynamics of electron-induced reaction according to the D-I2S model for dimethyldisulfide dimer, trimer, and tetramer on Au(111). As indicated, one delocalized electron was added to the dimeric chain and two electrons to the longer chains.

these molecular chains using the linear configuration appropriate to the adsorbed state but treating the system as a gaseous assembly; the result was a charge-distribution with approximately twice the charge on the end-atoms as in the body of the chain, as shown by the circled charges in Figure 4.

In Figure 5 the number of electrons required to induce the observed linear exchange reaction was $1\,e^-$ for the dimeric chain and $2\,e^-$ for the trimer and tetramer. The requirement for two added electrons in the case of the longer chains arose from the larger extent of delocalization which reduced the electron density and hence the dissociative impulse at each individual S–S bond. On this basis we expect a $1\,e^-$ chain reaction for two-member chains of dimethyldisulfide and a $2\,e^-$ chain reaction for three and four member chains.

We arrive at three conclusions:

1) Our "impulsive two-state" (I2S) model, embodying molecular dynamics on an ionic excited pes* for t^*, followed by extended dynamics on the ground pes, is able to account in detail for the observed dynamics[12,13] of the electron-induced reaction of a single physisorbed dimethyldisulfide dissociating to give a pair of chemisorbed thiyls on Au(111).

2) When applied to adjacent pairs of dimethyldisulfide molecules at the same surface, the model confirms the proposal of Maksymovych, Yates, and co-workers[14] that translationally 'hot' thiyl recoiling from the molecule that is electronically dissociated will collide forcefully with the neighboring molecule of the physisorbed line. However, this collision is a glancing one (impact parameter 2.14 Å), in addition to which the recoiling thiyl is strongly rotationally excited, with the result that no chain-reaction event (much less a series of them) was found. We therefore looked elsewhere (see below) for a physical explanation of the widespread electron-induced reconfiguration of linear dimethyldisulfide chains observed by Maksymovych, Yates et al.

3) We have introduced a new explanation of the experimental findings based on a generalizable extension of the I2S model to a distributed impulse model, D-I2S, in which a) the added charge coming from the STM tip instantaneously delocalized along the physisorbed dimethyldisulfide molecular chain by way of its antibonding orbitals to give the charge-distribution computed for the corresponding gaseous molecular ionic-chain, and b) during the time t^* spent in this ionic state, pes*, the fraction of the charge that resided on each S–S bond contributed a repulsive impulse at that S–S bond which, subsequently on the ground pes, severed the bond in favor of forming new differently aligned S–S and also two chemisorbed thiyls, thereby accounting for the change in conformation along the molecular chain, found by Maksymovych, Yates et al. Briefly stated, we have replaced these earlier workers' tentative hypothesis of a chain reaction by a model based on instantaneous charge flow that leads to widespread loosening of all the S–S bonds (the electron-induced "distributed impulse") and subsequently to concurrent reaction along the entire length of the chain. The event, according to this new model, is depicted for dimethyldisulfide tetramer in a movie in the Supporting Information.

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[20] The C–S bond direction in the thiyl radicals in our Figure 1 is in the same enantiomeric configuration as shown in Maksymovych et al.[14] Figure 1 panel A (monomer)and B (dimer), namely with the C–S bond pointing outward away from S–S. However, Maksymovych et al. showed a different configuration of thiyl in Ref. [14], Figure 1, panel C (tetramer); C–S was pointing inward toward S–S. We believe this different thiyl alignment was selected unintentionally, since the experimental STM images for the molecular chains did not clearly reveal the alignment of the terminal thiyl. The alignment of thiyl product computed in our work was found to be unchanged in going from monomer, to dimer, to trimer, and to tetramer, with C–S pointing outward away from S–S. We show this calculated C–S bond alignment in our Figure 1, in agreement with Maksymovych Figures 1 A and B in Ref. [14].

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