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Functional Thiols as Repair and Doping Agents of Defective MoS₂ Monolayers

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Abstract. Recent experimental and theoretical studies indicate that thiols (R-SH) can be used to repair sulfur vacancy defects in MoS₂ monolayers (MLs). This density functional theory (DFT) study investigates how the thiol repair mechanism process can be used to dope MoS₂ MLs. Fluorinated thiols as well as amine-containing ones are used to p- and n-dope the MoS₂ ML, respectively. It is shown that functional groups are only physisorbed on the repaired MoS₂ surface. This explains the reversible doping with fluorinated thiols.

Keywords: 2D materials, MoS₂ monolayer, doping, DFT, defect repair

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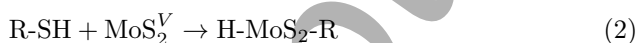
1. Introduction

In order to use 2-dimensional transition metal dichalcogenide (TMD) monolayers (MLs) as semiconducting materials in flexible field effect transistors (FETs) [1–3] or sensors[4–7] they need to be almost defect free. Here, especially the repair of sulfur vacancy (SV) defects is of interest because this defect introduces a defective state in the gap region slightly below the conduction band edge as shown in Reference [8], [9] and [10].

While this defective state is localized around the vacancy and thus, only the neighbouring molybdenum and sulfur atom of the SV defect are affected, it still considerably reduces the performance of MoS₂ ML based FETs,[9] and the photoluminescence.[11–13] Several experimental and theoretical studies have been performed to investigate how the SV defect can be healed.[14–16] The use of thiols (R-SH) has been discovered as a favorable method.[17–22]

In the present study the possibility to use the SV healing mechanism of thiols to not only repair the localized SV defect (cf. figure 1) but also to dope the MoS₂ ML at the same time is explored. For this purpose the alkyl chains of the thiols are replaced by functional groups such as perfluorocarbons and amines for p- and n-doping, respectively. The fluorinated thiol CF₃(CF₂)₉(CH₂)₂-SH and the amine-containing one NH₂(CH₂)₂-SH have already successfully been used in an experimental investigation.[23]

Three different repair and functionalization reactions that have been proposed in the literature[20–22] are investigated for their doping efficiency.

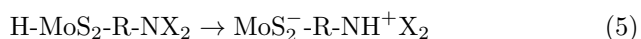


In reaction 1 the thiol R-SH repairs the SV defect of MoS₂ (MoS₂^V) by inserting the missing sulfur atom and then forming R-H, which is physisorbed on the MoS₂

surface. Any resulting modification of the electronic structure of MoS₂ is due to the physisorbed R-H molecule, and the MoS₂ ML itself exhibits no SV defect.

In reactions 2 and 3, on the other hand, the formation of a chemical bond between the functional group R and the MoS₂ ML may create new states in the gap region, which can be viewed as dopant states. The difference between reaction 2 and 3 is that in reaction 2 the residual hydrogen atom from the SH-group forms a chemical bond with one of the molybdenum atoms of the original SV defect (H-MoS₂-R). In reaction 3 this hydrogen atom instead reacts with a second hydrogen atom, forming the gas H₂ that leaves the MoS₂ surface. Thus, only the residual R remains chemically connected to the MoS₂ surface (MoS₂-R).

In the case of amine-containing thiols, SH-R-NX₂, where X stands for hydrogen atoms and/or methyl groups, a protonation of the amine NX₂ had been identified as the driving force of the n-doping effect in an experimental study for similar n-doping amines on a different substrate.[24] With the help of Kelvin probe microscopy, it was found that about 40 % of the amines were ionically protonated. The same may be true for the doping of MoS₂ surfaces. Sim *et al.*[23] observed that the n-doping effect of amine-containing thiols depends on whether the experiment is performed in ambient condition or in N₂ atmosphere. In the case of reaction 1, the product H-R-NX₂ might be protonated through a reaction with adsorbed water molecules as shown in reaction 4 in ambient conditions. The product of reaction 2, on the other hand, does not require water to protonate the amine. Here the hydrogen atom that is bound to the molybdenum atom of the SV defect can move to the amine group NX₂ to create NHX₂ as shown in reaction 5.



In the present study we investigate the influence of different functional groups R. Density functional theory (DFT) is employed to study all three possible reactions of fluorine and amine-containing thiols. The

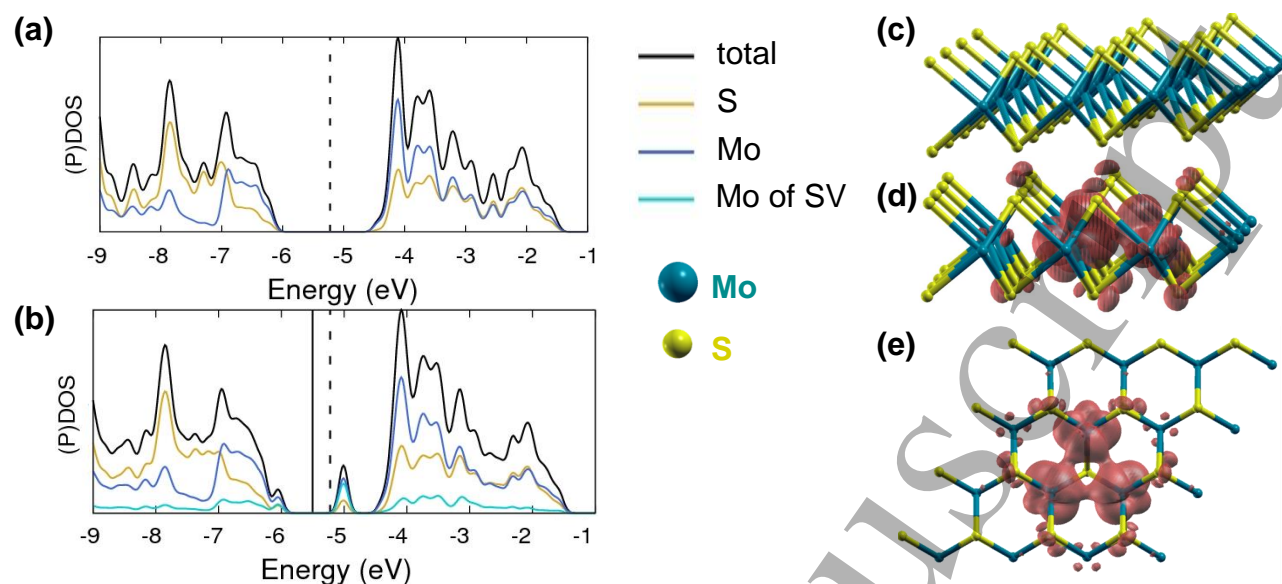


Figure 1. (a) The (P)DOS of the perfect MoS₂ ML. (b) The (P)DOS of MoS₂ with a SV defect. (c) Side view of the perfect MoS₂ ML. (d) Side view and (e) top view of the supercell of MoS₂ with a SV defect with the spatially resolved LDOS of the defective state around -5 eV highlighted in red. The solid vertical black line in the PDOS is the Fermi level of the defective MoS₂. The dotted black line shows the Fermi level of the defect free MoS₂ for comparison. All DOS and PDOS functions have been convoluted by a Gaussian with a full-width at half maximum of 0.1 eV. The isovalue of the LDOS plot is 0.003e/bohr³.

energetically favorable reaction out of the three above ones is determined. Further, the strength of the doping is investigated for each individual reaction and functional thiol. In case of the amine-containing thiol, the role of protonation is also studied.

2. Theoretical Methods

DFT calculations were performed with the SIESTA code, version 3.2.[25] The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [26] was employed together with a double- ζ plus polarization basis set (DZP). A periodic structure of MoS₂ was used. The MoS₂ educt with a sulfur monovacancy consisted of 16 molybdenum and 31 sulfur atoms (cf. figure 1(d) and 1(e)) and a vacuum region of approximately 30 Å between the MoS₂ layers. A fine grid [27] of 4×4×1 k -points in the Brillouin zone and its equivalent in supercells was used to sample the reciprocal space of the MoS₂ model system. The supercell had the lattice vectors $\vec{a}_1 = (12.84, 0.00, 0.00)$ Å, $\vec{a}_2 = (6.48, 11.12, 0.00)$ Å, $\vec{a}_3 = (0.00, 0.00, 36.11)$ Å. Depending on the examined thiol the resulting vacuum region in z -direction decreases to 18 Å or 25 Å for the fluorine and amine containing thiol, respectively.

The geometries of the doped MoS₂ MLs have been optimized with the conjugate gradient method,[28] until none of the forces exceeded 10⁻² eV/Å. A mesh

cutoff of 200 Ry was used. All atoms have been described by Troullier-Martins pseudopotentials, [29] obtained from the on-line resource in Reference [30]. The pseudopotential of sulfur has been generated without core corrections using the ATM code in the SIESTA suite and the parameters listed in Reference [30].

3. Results and Discussion

3.1. Fluorine-containing Thiols

First, the doping with fluorine-containing thiols is studied. In their experiment the group of Sim *et al.*[23] observed a p-doping effect for the fluorinated thiol CF₃(CF₂)₉(CH₂)₂-SH after it repaired a MoS₂ ML with SV defects. With CF₃(CF₂)₇(CH₂)₂-SH our model fluorine-containing thiol (cf. Figure 2) is slightly shorter but still comparable to the thiols used by Sim *et al.* In Figure 2 the three competing defect repair and doping reactions, denoted with **a** for the fluorine-containing thiol, with their associated reaction energies are shown.

From the three reactions, reaction **1a** is clearly the thermodynamically preferred one with a reaction energy of -3.19 eV. The energetically least favorable among the three investigated reaction is reaction **2a**

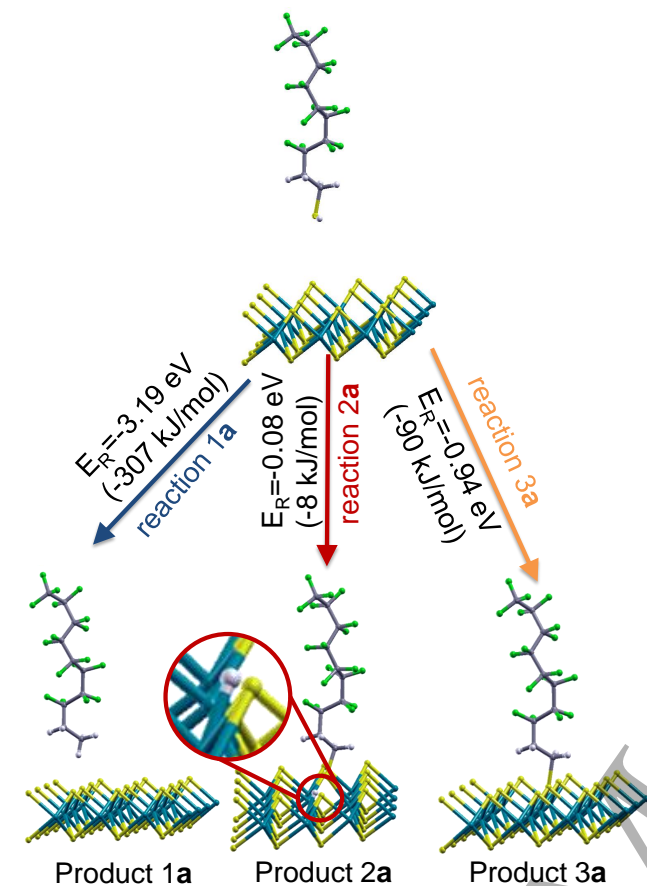
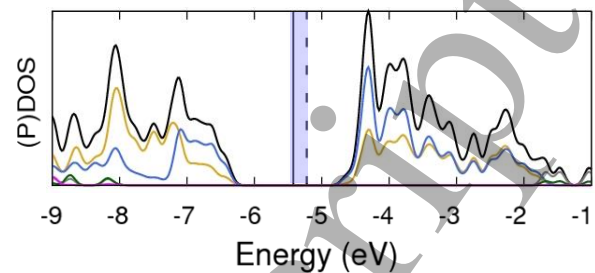


Figure 2. The three different reaction pathways that the $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{-SH}$ molecule can take when it reacts with a MoS₂ ML with a SV defect. The circle highlights the position of the hydrogen atom that is bound to the molybdenum atom of the SV defect in product 2a.

with a reaction energy of -0.08 eV. Reaction 3a has a reaction energy of -0.94 eV. It has been shown in reference [20] that reactions 1 and 2 share the same transition state, which leads to the conclusion that out of the three reactions shown in figure 2 reaction 1a will be the one that takes place when the fluorine-containing thiol reacts with a MoS₂ ML with a SV defect.

The corresponding (P)DOS of the products of reactions 1a and 2a (cf. Figure 3) provide information on their doping effect. Here it is important to distinguish between a doping effect with reference to the Fermi level of the perfect MoS₂ ML (dotted line in the PDOS) or with reference to the real system for which reference [23] discusses an experimentally observable doping effect. In the latter case, a n- or p-type doping effect would be determined based on the Fermi level of the SV defect containing MoS₂ ML. Depending on the percentage of the SV defects, the reference Fermi level would lie between the Fermi level of the perfect

(a) Product 1a



(b) Product 2a

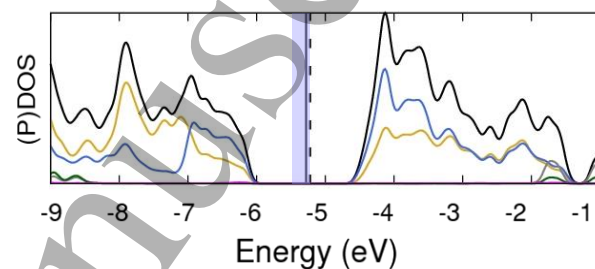


Figure 3. The DOS and PDOS of the product of (a) reaction 1a, (b) reaction 2a with the fluorinated thiol. The vertical solid line shows the Fermi level of the doped MoS₂ layer, whereas the dotted black line indicates the Fermi level of the defect-free MoS₂ layer as a reference and the soft purple area indicates the probable span of the Fermi level in an experiment. All DOS and PDOS functions have been convoluted by a Gaussian with a full-width at half maximum of 0.1 eV.

MoS₂ ML and the SV defect containing MoS₂ ML (cf. figure 1(c) for a SV defect percentage of 2.1%). The resulting range of the Fermi level in the experiment is displayed as a purple area in the PDOS figures.

Figure 3a shows the PDOS of the product of reaction 1a, confirming the experimentally observed p-doping effect of fluorine-containing thiols. The position of the Fermi level in figure 3(a) visualize this effect. It can be seen that the Fermi level of the product of reaction 1a (solid line) is energetically lower than the Fermi level of the perfect MoS₂ ML (dashed line). In detail, the physisorbed product 1a shifts the energy of the valence band from -6.18 eV in a perfect MoS₂ ML to -6.38 eV in the product 1a. Thus, a p-doping effect can be observed. This is analogous to the doping of semiconducting polymers. [31]

With reference to the experiment by Sim *et al.*, the Fermi level of the product of reaction 1 lies at the edge of the estimated range for the Fermi level of

the experimental MoS₂ ML, indicating a weak p-type doping with reference to the SV defect containing MoS₂ ML. This is in agreement with the observation of a weak p-type doping effect by Sim *et al.*

While from a thermodynamical point of view reaction 2a is the least likely one, reference [21] attributes the observed doping in the experiment to the product 2a.[23] For testing this hypothesis we calculated the DOS of reaction 2a and display it here. However, our results (cf. Figure 3(b)) do not support such an explanation. The energy of the valence band edge of the product is nearly identical with a difference <0.01 eV. However, the band gap is reduced from 1.91 eV to 1.78 eV. This indicates no doping with respect to the perfect MoS₂ ML and a n-type doping with respect to the experimental SV defect containing MoS₂ ML. With regard to the discussion in reference [21] that product 2a would lead to a p-type doping, we would rather correlate it to a shift in optical absorption studies.

It can be concluded that only reaction 1a leads to the experimentally observed p-doping effect for fluorine-containing thiols without a reduction of the band gap. The reaction energies of all three reactions support this conclusion, as among the three reactions considered here, reaction 1a is the most exothermic one and thus the dominant reaction that should take place. Further, in the experiment a significant reduction of the p-doping was observed after the annealing process. This could be explained by the removal of the physisorbed products 1a, which have only an absorption energy of 0.01 eV to the surface of the perfect MoS₂ ML.

3.2. Amine-Containing Thiols

An n-doping effect has been reported for amine-containing thiols in reference [23]. For the model amine-containing thiol N(CH₃)₂(CH₂)₃-SH (cf. Figure 4) again all three possible reactions 1–3, denoted with **b** for the amine, were studied to see if the amine head group changes the reaction preference. Figure 4 shows that the general trends for reactions 1b–3b are almost identical to the fluorine-containing counterparts (cf. Figure 2). In detail, the reaction energies are -3.09 eV, 0.19 eV and -0.90 eV for reactions 1b–3b, respectively.

With regard to the n-doping effect, here again only reactions 1b and 2b are analysed. Figure 5(a) and (b) show the PDOS and Fermi level for both reactions (1b, 2b). It can be seen that reaction 1b does not lead to the desired n-doping with reference to the perfect MoS₂ ML. The reason for this is that the new

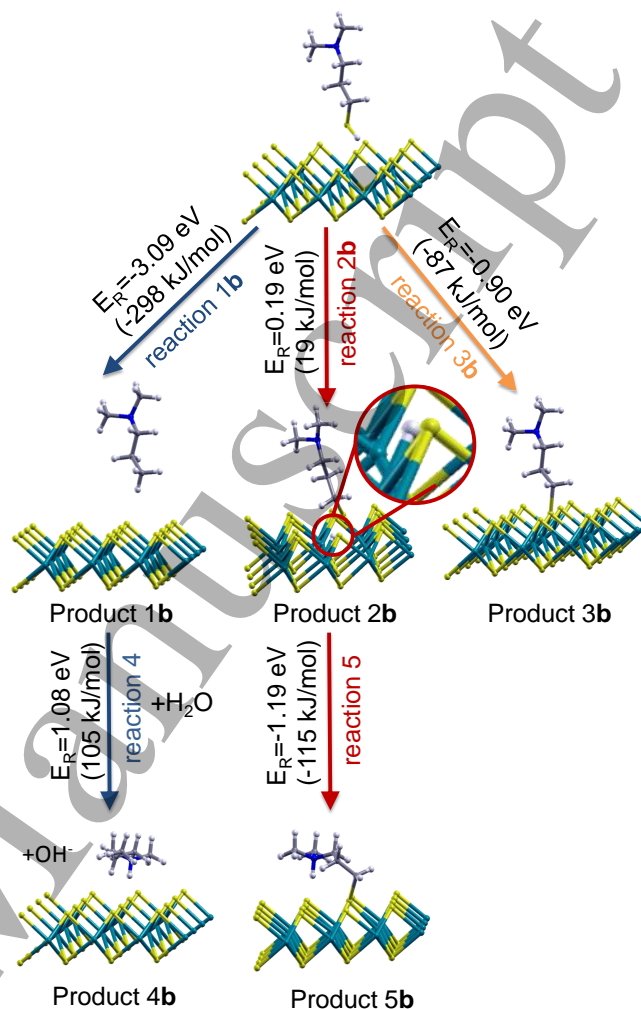


Figure 4. The three different reaction pathways that the N(CH₃)₂(CH₂)₃-SH molecule can take when it reacts with a MoS₂ ML with a SV defect, as well as the two follow-up protonation reactions.

occupied state at around -5 eV is exclusively localized at the NH(CH₃)₂(CH₂)₂CH₃ molecule, *i.e.* there is no indication of a chemical bond. The spatially resolved representation of the state in figure 6(a) illustrates this localisation. Therefore, this new state cannot be considered as part of the valence band of the MoS₂ ML and has to be excluded when calculating the Fermi level of MoS₂. This results in a Fermi level and a valence band identical to the perfect MoS₂ ML and thus, no n-doping can be observed for reaction 1b with reference to the perfect MoS₂ ML.

With reference to the experiment and the initial SV defect containing MoS₂ ML (cf. purple area in figure 5(a)) an increase of the number of charge carriers that equals a p-type doping should be observed due to the repair of the SV defect. This is in agreement with the experimental observation by Sim *et al.*[23]

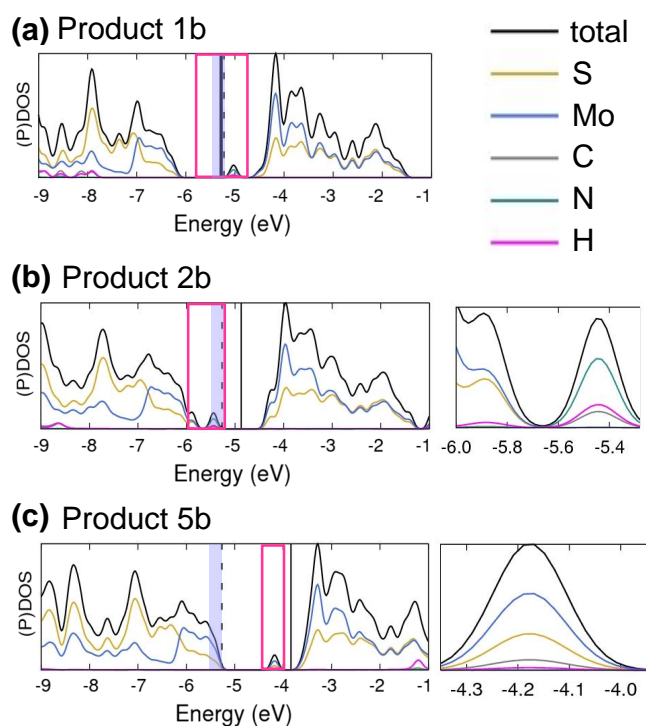


Figure 5. The DOS and PDOS of (a) the product of reaction 1b, (b) product of reaction 2b and (c) the product of the protonation reaction 5b with an amine-containing thiol. The insets in (b) and (c) show a detailed view of the PDOS of the new states of the products 2b and 5b. The vertical solid black lines shows the Fermi level of the doped MoS₂ layer, whereas the dotted black line indicates the Fermi level of the defect-free MoS₂ layer as a reference and the soft purple area indicates the probable range of the Fermi level in an experiment. All DOS and PDOS functions have been convoluted by a Gaussian with a full-width at half maximum of 0.1 eV.

Reaction 2b, on the other hand, shows a clear n-doping effect with reference to the perfect and SV defect containing MoS₂ ML. In detail, the Fermi level is moved by 0.4 eV towards the conduction band. This is mainly due to newly occupied state of the amine group at around -5.5 eV. Here, in contrast to reaction 1, the new state of the amine can be clearly assigned to the valence band of the MoS₂ ML. Due to bond between the amine and the MoS₂ ML the valence band of the MoS₂ ML is widened from -6.2 eV to -5.9 eV (cf. the inset of Figure 5(b)). Therefore, it can be concluded that both reactions 1b and 2b verify the experimentally observed n-doping with respect to the SV defect containing MoS₂ ML. With respect to the perfect MoS₂ ML, on the other hand, only reaction 2b would lead to an n-type doping.

However, as mentioned in the introduction, under ambient conditions a protonation of the amine is suggested to be the source of the n-doping effect. In case of reaction 1b the follow-up protonation reaction 4b could take place in ambient conditions. Reaction

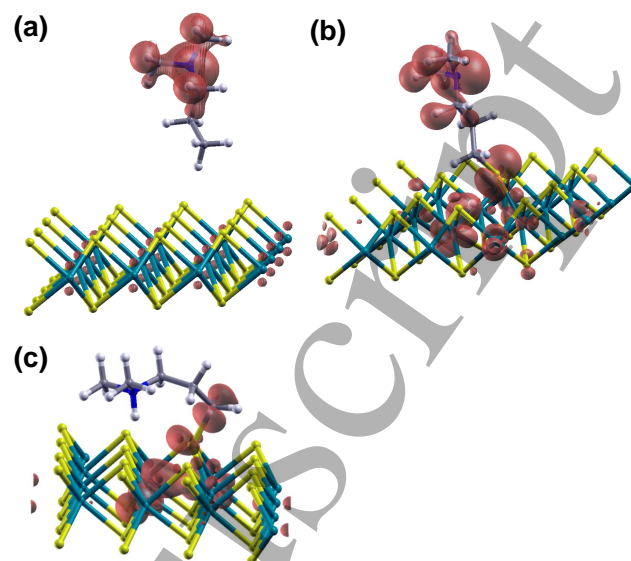


Figure 6. The spatially resolved representation of the LDOS shown in Figure 5 highlighted in red of (a) the product of reaction 1b, (b) the product of reaction 2b and (c) the product of reaction 5b. The isovalue of the LDOS plot is 0.003e/bohr³.

5b, on the other hand, would occur after reaction 2b. Both protonation reactions are shown at the bottom of Figure 4.

In case of reaction 5b the internal movement of the hydrogen atom from the SV defect to the amine group is clearly exothermic with a reaction energy of -1.19 eV (cf. figure 4). It shows a strong n-type doping due to a new occupied state at -4.19 eV. The spatially resolved representation of the valence band in figure 6(c) shows that the state at -4.19 eV is localized around the original SV defect. However, the resulting combined reaction energy of reactions 2b and 5b is still thermodynamically unfavorable compared to reaction 1b. This means that a protonation can only take place after reaction 1b.

Reaction 4b is an exemplary protonation reaction of a water molecule with the product of reaction 1b. In reference [32] the solvation free energy for the formation of OH⁻ is reported to amount to -4.6 eV. Under ambient conditions the alkylamine would act as a base in the presence of water molecules, which could lead to a protonation of the amine group. While similar to reaction 5b an increase of the n-type doping could be observed, due to the endothermic nature of the process with a reaction energy of 1 eV (cf. figure 4) such a protonation reaction is reversible under ambient conditions. This explains why a decrease of the p-type doping over time was observed by Sim *et al.* in ambient condition. In ambient condition the protonation of the amines would be reversed over time which leads to the

decrease of the measured p-doping.

In summary reaction 2b and the follow up protonation in 5b, as well as a protonation similar to reaction 4b would lead to n-doping effects with reference to the perfect MoS₂ ML. However, based on the reaction energies, reaction 1b is the reaction that should be observed. Here, a n-type doping could be determined with reference to the SV defect containing MoS₂ ML that is used in experiments.

4. Conclusions

Three different reactions to repair and functionalize MoS₂ MLs with a SV defect were investigated for two model thiols that contained either fluorocarbons or amines as the functional groups. The similar reaction energies of reactions 1–3 for both the fluorine and amine-containing thiols, as well as the energies reported in reference [20] and [21] for methylthiol suggest that the reaction energies for reactions 1–3 are independent of the residue R of the thiol R-SH. Reaction 1 for which the R-H molecule is physisorbed after the insertion of the missing sulfur atom is the dominant reaction path for thiols on MoS₂ surfaces with a SV defect.

Further, it was shown that based on the reaction energies and the doping effect, reaction 1 is the reaction that was most likely observed in the experiment of Sim *et al.*[23] as only this reaction resulted in the observed p-doping effect for the fluorinated thiol. The very weak physisorption of the product of reaction 1a explains why after the annealing the p-type doping effect is decreasing again in the experiment.

In case of the amine-containing thiol, reaction 2b and the protonated products of reaction 4b and 5b lead to a n-doping of the perfect MoS₂ ML. However, due to its strong exothermicity, reaction 1b should still be dominant and consequently lead to an n-doping through the repair of the SV defects in the MoS₂ ML.

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