Lateral MoS2 Heterostructure for Sensing Small Gas Molecules

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ABSTRACT: The potential of a two-dimensional (2D) molybdenum disulfide (MoS2) lateral heterostructure in sensing small gas molecules is being assessed on the basis of quantum mechanical calculations. This heterostructure combines two phases of MoS2, namely, a metallic ribbon embedded within the semiconducting MoS2 phase. In this work the influence on the electronic structure of this 2D material due to the adsorption of gas molecules is investigated. Specifically, the adsorption of NO, NO2, O2, CO, and CO2 on the MoS2 heterostructure is studied. Overall, gas-specific peaks in the electronic features of the 2D material could be clearly revealed, while differences were also found for a gas adsorption close to the interfaces of the material. The “poisonous” nitrogen oxide molecules showed a stronger adsorption on the material but could very well be distinguished over the “healthy” molecular oxygen gas. The complexity of the heterostructure provides more rich gas adsorption characteristics over the single-phase material and is thereby expected to show an enhanced sensitivity due to the increased statistics and the wider window of gate voltages that can be applied. This work provides a proof of principles on the high relevance of the 2D MoS2 heterostructure in view of response materials in gas detectors.

KEYWORDS: MoS2 heterostructures, 2D materials, DFT, electronic properties, gas molecules

INTRODUCTION

Two-dimensional (2D) materials have been intensively studied in the past years due to their high potential for novel nanotechnological applications. These materials include, among others, the 2D transition metal dichalcogenides (TMDCs). These are structures with the chemical formula MX2, where M is a transition metal such as V, Mo, and W and X is one of the chalcogens such as S or Se. Two-dimensional TMDC materials can be extracted from the bulk through mechanical exfoliation, chemical exfoliation, physical vapor deposition, and solution synthesis. These quasi-2D layered materials show a strong interlayer ionic-covalent bonding and weak out-of-plane interactions. Depending on their exact atomic arrangement and the positioning of the chalcogen X atoms, the 2D TMDCs can be found in distinct phases, such as a stable semiconducting (2H) phase with a direct band gap and a metastable metallic (1T) phase. The induced transformation from 2H to the 1T phase can be controlled by opening up routes for an atomically precise fabrication of single-layered chemically homogeneous electronic devices. In addition to this, 2D materials can form lateral heterostructures in which both metallic and semiconducting phases can coexist. The combination of different chemical structures or different phases gives rise to novel materials with unique properties. These include excellent mechanical flexibility, optical transparency, and favorable transport properties for realizing electronic, sensing, and optical systems on arbitrary surfaces. For example, MoS2 monolayers have shown a high potential as a key element in sensing devices. Specifically for gas sensing, semiconducting metal oxide based materials are typically used. However, these include a high temperature operation, long recovery time, low stability, and poor selectivity that may limit their practical use. In view of these drawbacks and the need for a higher sensitivity, new materials have been investigated. These include low-dimensional materials such as graphene sheets, graphene nanotubes, and semiconducting nanowires, but also TMDC monolayers and other 2D heterostructures. In 2D structures, the high surface-to-volume ratio is expected to promote specific binding or adsorption on their surface and enhance their potential as an essential component in sensors. In addition, exploring the possibility of combining the different phases provides another parameter for tuning the sensing properties of a 2D heterostructure. Motivated by these studies and the high exploration potential of 2D TMDC heterostructures, here we focus on a lateral MoS2 hybrid monolayer made of a metallic (1T) ribbon embedded in the semiconducting (2H) phase. Due to the strong anisotropy in the electronic properties of this hybrid material, which was assigned to its structural asymmetry found at the interfaces, it is possible to tune its electronic conductance.
efficiency and potential for identifying these molecules will be examined through the modulation in the electronic properties of the material. A key aspect for this is the molecules/material interactions at the interfaces between the semiconducting and metallic parts of the MoS2. Accordingly, this work is organized as follows: we begin with the description of the computational methodology used and continue with the presentation of the results on the gas absorption, as well as the electronic properties of the 2D hybrid heterostructure interacting with the gas molecules. In the end, we discuss the sensitivity of this material in view of novel 2D sensors.

**METHODOLOGY**

This work is a computational study based on density functional theory (DFT)\(^45,46\) as implemented in VASP.\(^47\) Self-consistent supercell calculations are performed using the optB86b-vdW van der Waals (vdW) exchange–correlation functional\(^48\) with accurate frozen-core full-potential projector augmented wave (PAW) pseudopotentials. The choice of a functional that takes into account dispersion was made in order to account for any—even small—van der Waals interactions between the molecules and the 2D material. No dipole corrections are made, as the 2H edges of the material are similar and symmetric, while in-plane different Mo positions in the 1T phase cannot generate a significant asymmetry in the slab that induces a large out-of-plane dipole moment. The k-space dimension and the plane-wave basis functions were chosen to ensure that the total energy is converged at 1 meV/atom. A Monkhorst–Pack k-point mesh was employed for the Brillouin zone integration, with a 450 eV energy cutoff for the wave functions. The lattice vectors as well as the atom coordinates are relaxed with the tolerance of less than 0.01 eV/Å on each atom. The calculations for the 1T/2H MoS2 were performed at the Γ with a mesh of 12 × 4 × 1. We have first tested our method for the pristine 2H MoS2 monolayer, which resulted in a Mo–S bond length of 3.16 to 3.23 and an electronic band gap of 1.75 eV. The latter was found in good agreement with the experimental values of 1.8—1.9 eV and the computational value of 1.6 eV.\(^42\) For the hybrid 1T/2H MoS2, the starting point of our simulations was the 132 sulfur and 66 molybdenum atom hexagonal supercell with 6 units of 1T embedded in 2H taken from a previous study.\(^17\) In the following, the notation 1T/2H MoS2 will be used for this 2D structure. We have further relaxed this with our method and obtained the same electronic properties for the pristine material as shown before.\(^17\) The resulting hybrid monolayer illustrated in Figure 1 reveals Mo–S bond lengths in the range of 2.3–2.5 in its 1T phase.

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**Figure 1.** Different views of the 2D 1T/2H MoS2 structure as denoted by the labels. The two phases, 2H and 1T, are also denoted and point to the two interfaces in the material. The latter are clearly shown through the red lines on the side view. A NO molecule is shown at different positions on top of 1T/2H MoS2 in order to point to the scanning procedure (see text). The labels “2H”, “IF1”, “1T”, and “IF2” correspond to distinct positions discussed further (see Results and Discussion). Note that only one molecule at a specific site is taken into account for each calculation. The distance \(d_{\text{MO}}\) between the mid-distance in the molecule and the nearest Mo atom of the monolayer is denoted on the lower panel. The sulfur, molybdenum, oxygen, and nitrogen atoms are depicted in yellow, cyan, red, and blue, respectively. The same color coding will be used throughout.

**Figure 2.** Different adsorption sites considered in this study shown for the 2H phase. In panel a, the sites on a Mo–S hexagonal ring are sketched. In panel b, the labelings for the different orientations of the planar molecules are given, while panel c shows the case of the nonplanar NO\(_2\) molecule and the respective labels for the adsorption sites. In panels b and c, the orientations are shown for an adsorption on the M site in panel a. In panel c, the axes are also given for reference.
Our focus is the adsorption of small gas molecules on 1T/2H MoS$_2$. Of those, we consider the five molecules O$_2$, CO, CO$_2$, NO, and NO$_2$ and perform a structural optimization of these. For these optimizations, an electronic energy convergence of $10^{-7}$ eV/Å and a force tolerance of 0.001 eV/Å were used. All gas molecules relaxed at a bond length slightly longer than the experimental values, but in a very good agreement with earlier DFT calculations. As a starting point and in order to find the preferred adsorption sites, we use the 2H phase as a reference and place each molecule separately on top of this single-phase material. In order to evaluate the preferred adsorption sites, the molecules are placed on top of the Mo–S hexagonal ring at different sites as shown in Figure 2a: on the sulfur atom (“S”), on the molybdenum atom (“M”), on a hollow site (“H”), and on top of the Mo–S bond (“B”), as in previous studies. For these sites, we perform a scanning of the vertical distance between the closest atom of the molecule to the top S plane of the 2H monolayer. The different orientations of the molecules with respect to the 2D structure are also taken into account according to Figure 2b. For the nonplanar NO$_2$ molecule, additional orientations were considered as seen in Figure 2c. All these positions are labeled with respect to the molecule orientation and the adsorption site. The label “vO” indicates that the molecule lies vertically (v) to the monolayer with the oxygen (O) atom closer to the surface; “vN” denotes the same orientation with the nitrogen (N) atom closer to the surface; “h” represents the orientation with the molecule lying horizontally/planar (h) to the monolayer and parallel to the Mo–S bond in the y direction (y). Similarly, for NO$_2$ in Figure 2c, the label “MVxO” denotes an adsorption on the Mo site (M) with a vertical arrangement of the molecule (v), with the oxygen atoms (O) being closer to the material and the molecule pointing toward the x axis (x). Representative optimized geometries are shown in Figure 3: there a NO$_2$ molecule is adsorbed on and interacts with the 2H part of the 1T/2H MoS$_2$ structure. From such geometries for all molecules placed on top of the 2D material, we calculate the respective energetics and the electronic properties.

Through scanning of all these distances and sites, we obtain an energy map that reveals the site of strongest adsorption and the respective optimum distance of the molecule from the 2H material. At this optimum distance for each molecule, its adsorption energy to the 2D structure is calculated through

$$E_{\text{ads}} = E_{\text{gas}/2\text{D}} - E_{2\text{D}} - E_{\text{gas}}$$  (1)

where $E_{\text{gas}/2\text{D}}, E_{2\text{D}},$ and $E_{\text{gas}}$ are the total DFT energies for the system of the adsorbed molecules and the 2D material, the isolated 2D structure, and the isolated gas molecule, respectively. On the basis of these findings, at a second step, we place the gas molecules on top of 1T/2H MoS$_2$ at the preferred sites and distances. For this part, the molecule–monolayer distance is kept fixed and the effect of the gas molecules on the electronic properties of the 1T/2H MoS$_2$ structure are investigated. Specifically, we perform scanning along the material, as shown in Figure 1. Accordingly, each molecule is placed on top of a certain site and is being moved along the hybrid material, always remaining on top of a similar site. In this way, it moves in distinct steps from the 2H phase across the interface to the 1T phase and then crosses one more interface to the 2H phase on the right of this figure. Single-point calculations were performed for all molecules on the depicted sites. Note that additional orientations and sites could be taken, also for the 1T or hybrid structures. However, as it is not possible to include all of this information, we have chosen some very representative cases as a proof of principles.

### RESULTS AND DISCUSSION

**Adsorption on 2H MoS$_2$.** We begin the analysis with the gas adsorption on the pristine 2H phase, which will be used as a reference. This part serves as a simple case for performing the adsorption site search and optimization of the gas—structure distance, as discussed above. From the results it was clear that the strongest adsorption site for most gas molecules is the M site and the hx orientation (VxO for NO$_2$). Qualitatively, our findings on the preferred adsorption order are in good agreement with previous studies. Deviations from some of the literature results (e.g., H site found more stable for CO) are based on the less accurate LDA exchange–correlation functionals used previously. In those cases, the results presented here are more reliable due to the higher level of theory used here. Note, though, that, for a similar level of theory as ours, it was shown that the CO$_2$ molecule is adsorbed on a site between the M and H sites and much closer to the M site with the respective adsorption energy in the range of $-0.14$ and $-0.25$ eV for different vdW corrected exchange–correlation functionals. This energy from our simulations was found at $-0.19$ eV (Table 1). The distance of the molecule

### Table 1. Adsorption energies ($E_{\text{ads}}$) of the Different Gases with an hx (VxO for NO$_2$) Orientation on the M Site of the 2H MoS$_2$ and Their Respective Distance ($d_{\text{ads}}$) from the Nearest S Atom of the 2H MoS$_2$

<table>
<thead>
<tr>
<th>gas</th>
<th>$E_{\text{ads}}$ (eV)</th>
<th>$d_{\text{ads}}$ (Å)</th>
<th>$\Delta n$ (e$^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>$-0.138$</td>
<td>3.2</td>
<td>0.016</td>
</tr>
<tr>
<td>CO</td>
<td>$-0.144$</td>
<td>3.4</td>
<td>0.008</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$-0.188$</td>
<td>3.2</td>
<td>0.017</td>
</tr>
<tr>
<td>NO</td>
<td>$-0.204$</td>
<td>3.0</td>
<td>0.012</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>$-0.226$</td>
<td>3.0</td>
<td>0.049</td>
</tr>
</tbody>
</table>

The charge redistribution $\Delta n$ in all cases is also given.
from the material was previously found at 3.18 Å,42 while in our case this distance was 3.2 Å (Table 1). Accordingly, the results are very close and any small differences are based on the level of vdw theory and relaxation. In that respect, both results discussed for CO2 are reliable within the accuracy of the exchange–correlation functionals. Accordingly, we have considered for this molecule the positions hx and hy at the H site,42 as well as the hx position at the M site. As no significant deviations (larger than 2 meV) were found for these cases, we have further considered the M site for CO2 to be consistent for all molecules. Selected energetics arising from the site/distance scanning are summarized in Figure 4. The comparison of all gas molecules adsorbed at the M site shows that NO2 is better adsorbed than all other molecules, while the less stable adsorption was found for O2. The strongest adsorption of the NO2 molecule is also related to a shortest distance to the 2D material. In this context, NO2 is better adsorbed than all other molecules. Accordingly, we have performed a Bader charge analysis.53,54 The respective charge redistribution is defined as Δn = n_{ads} – n_{iso} where n_{ads} and n_{iso} are the charge densities of the adsorbed and isolated gas molecule, respectively. Accordingly, for Δn > 0, electrons are moving from the MoS2 to the gas molecule, while the opposite occurs for Δn < 0. According to the table, all Δn > 0 point to the fact that part of the electrons on the material move toward the adsorbed molecule.

The redistribution of the charge in the system of the adsorbed molecules and the 2H structure alters the electronic structure of the pure 2H. The presence of a gas molecule actually introduces additional electronic states to the total gas/material system. In order to reveal possible differences of these modifications, we take the electronic density of states (eDOS) as a representative quantity. The different contributions of the gas molecules to the total eDOS of the combined molecule/material system are depicted in Figure 5. These reveal gas-specific peaks at very distinct energy ranges. Interestingly, the peak of the “healthy” gas O2 is well separated from the poisonous nitrogen oxides or the carbon monoxide ones. Apart from the NO peaks, all other electronic states related to the gas molecules are outside the band gap of the 2H phase. In the end, as previously shown,42 2H MoS2 reveals a distinct electronic behavior for different gas molecules. We next aim to show, that this specificity holds and can be enhanced by using the 1T/2H MoS2 heterostructure as a sensor component. **Adsorption on 1T/2H MoS2.** We move on with the gas adsorption on hybrid 1T/2H MoS2. In this process the gas molecules were initially positioned on top of the 2H phase on
Figure 5. Total electronic density of states (eDOS) for the pure 2H material compared to the contribution to the eDOS of the gas molecules in the adsorbed gas/2H MoS2 system. Adsorption on the M site is considered here. All energies are shifted with respect to the valence band (VB) of the pure 2H phase (E_{VB(pure2H)}), which was set at 0 eV.

Table 2. Adsorption Energies, the Respective Distance of the Gas Molecule from the Surface (d_{ads}), and Charge Redistribution for All Gas Molecules Adsorbed on the Hybrid 1T/2H MoS2

<table>
<thead>
<tr>
<th>position</th>
<th>2H</th>
<th>IF1</th>
<th>1T</th>
<th>IF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2 (d_{Mo} = 4.75 Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_{ads} (eV)</td>
<td>−0.138</td>
<td>−0.139</td>
<td>−0.131</td>
<td>−0.118</td>
</tr>
<tr>
<td>Δn (e−)</td>
<td>0.015</td>
<td>0.014</td>
<td>0.016</td>
<td>0.027</td>
</tr>
<tr>
<td>CO (d_{Mo} = 4.95 Å)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_{ads} (eV)</td>
<td>−0.142</td>
<td>−0.143</td>
<td>−0.138</td>
<td>−0.126</td>
</tr>
<tr>
<td>Δn (e−)</td>
<td>0.008</td>
<td>0.008</td>
<td>0.010</td>
<td>0.008</td>
</tr>
<tr>
<td>CO2 (d_{Mo} = 4.75 Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_{ads} (eV)</td>
<td>−0.184</td>
<td>−0.210</td>
<td>−0.206</td>
<td>−0.134</td>
</tr>
<tr>
<td>Δn (e−)</td>
<td>0.016</td>
<td>0.018</td>
<td>0.021</td>
<td>0.015</td>
</tr>
<tr>
<td>NO (d_{Mo} = 4.55 Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_{ads} (eV)</td>
<td>−0.232</td>
<td>−0.246</td>
<td>−0.286</td>
<td>−0.208</td>
</tr>
<tr>
<td>Δn (e−)</td>
<td>−0.092</td>
<td>−0.076</td>
<td>−0.120</td>
<td>−0.079</td>
</tr>
<tr>
<td>NO2 (d_{Mo} = 4.55 Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_{ads} (eV)</td>
<td>−0.189</td>
<td>−0.226</td>
<td>−0.222</td>
<td>−0.144</td>
</tr>
<tr>
<td>Δn (e−)</td>
<td>0.040</td>
<td>0.039</td>
<td>0.045</td>
<td>0.056</td>
</tr>
</tbody>
</table>

the adsorption for the different material parts without revealing a specific trend. The anisotropy of the two interfaces is mapped on the adsorption energies, which differ when placing the molecule on these interfaces. Overall, the right interface shows a less stable adsorption compared to the left one. The adsorption energies related with the 2H part of the material are very close to those of the pure 2H given in Table 1, with some tiny deviations denoting the presence of the interface. O2 and CO show a preference in binding on the 2H or the IF1 parts, CO2 and NO2 to the IF1 and 1T part, while NO shows a much higher adsorption on the 1T part of the 1T/2H MoS2. The charge redistribution is similar to the adsorption on the 2H material apart from the nitrogen oxide molecules, which slightly increase toward the 1T part. The nitrogen oxides show the highest charge redistribution. Compared to the other molecules, in the NO2 case, on average about three times more charge moves toward the molecule when adsorbed on 1T/2H MoS2. Interestingly, for NO adsorbed on 1T/2H MoS2, the charge not only increases but also moves toward the material as denoted by the negative signs of Δn. Finally, NO2 and O2 show the highest charge redistribution at the weakest adsorption site, while for NO the opposite behavior was observed.

On the basis of these observations, we next focus on the electronic behavior of the gas/material system through the analysis of the various eDOS. A comparison of the total eDOS (not shown) for all gas molecules placed at different positions on top of 1T/2H MoS2 reveals high similarities. Only small variations for the same positioning and the different molecules or the same molecule at different positions can be identified. In order to better identify the influence of the gas states on the total electronic behavior of the gas/material system, a direct comparison of these states to the total eDOS is depicted in Figure 6. The results are shown for the two dioxide gases (CO2 and NO2) placed at different positions. As a first comment, the total eDOS does not change with respect to the different gas positioning, apart from the energy range corresponding to the peaks arising from the gas molecules. Interestingly, the CO2 peaks are static with respect to the various gas positions on top of the 1T/2H MoS2. This is not the case for NO2, for which a different positioning of the gas on top of the 1T/2H MoS2 leads to a shift of the peaks. The largest shift toward higher energies was found for NO2 on top of the 1T part of the material. Note that for CO2 the different positions also correspond to different adsorption energies. However, the charge redistribution is about two times lower than for NO2 at the same positions. This could possibly justify the negligible shift of the CO2 peaks for the various gas positions.

In order to identify the response of the material itself to the adsorption and the presence of the gas molecules, we turn to the various contributions of the different elements in the eDOS. For this, the projected densities of states (PDOS) are depicted in Figure 7 for the two nitrogen oxides placed at the position 1T on top of 1T/2H MoS2. It can be clearly seen that the Mo and S components in the eDOS for both phases do not change with respect to the molecule. However, small modifications in the total eDOS of the combined gas/1T/2H MoS2 system can be seen. These arise only from the additional electronic states provided by the gas molecules. The latter are very distinct for the two molecules NO and NO2 and can be found at different energy ranges. At these energies small differences in the total eDOS are revealed when comparing the NO and NO2 adsorption.
Similar are the findings for the other molecules as well. In view of the applicability of 1T/2H MoS$_2$ as a gas sensor element, we next consider the comparison between a “healthy” and a “poisonous” gas. As representatives, we take O$_2$ and CO and compare the contribution of each gas molecule to the total eDOS of the combined gas/surface system, as shown in Figure 8. Again, the gas peaks in the eDOS are gas specific and can be found in distinct energy ranges. On top of this, the gas peaks are moving toward higher energies along the scanning direction on top of the 1T/2H MoS$_2$. For O$_2$, the peaks clearly move from lower energies when placed at the 2H position toward higher energies at the 1T and the interface positions. This effect is less pronounced in the CO adsorption with a shift of about 0.5 eV in the peaks and the different positions. The respective shift in the O$_2$ case is almost 2.5 eV. Accordingly, CO is not strongly influenced by the phase of the material, which is not the case for O$_2$. In view of sensing, an almost static peak would indicate a poisonous gas, while a spread peak distribution would denote that the gas is healthy. Inspection of all peaks for all molecules reveals quite distinct features. A comparison of the 2H and 1T positioning shows a clear shift of the peaks toward higher energies in all cases except the carbon oxides. Positioning close to the two interfaces also shows distinct features, mainly for O$_2$ and the nitrogen oxides. Interestingly, for CO$_2$ on top of the 1T phase, the eDOS peaks tend to vanish, and are significantly weaker on top of IF$_1$, where the adsorption is actually stronger. NO is the only gas which shows a splitting of the large peak closer to the Fermi level when comparing the 2H positioning with the other three. This can be possibly attributed to the different charge redistribution (see Table 2) compared to the other molecules, which indicates a different interaction with the underlying material. No evidence can be provided from the simulations. This point is rather based on physical intuition. For NO, charge is moving toward the material. As the 2H part is semiconducting, the peak seen on the top left panel in Figure 8

![Figure 6. Total DOS and the contribution from the gas molecules. The results are shown for the CO$_2$ (left) and the NO$_2$ (right) gas molecules, respectively. The gas molecules are separately positioned on top of the 2H (“gas@2H”, solid lines), the 1T (“gas@1T”, dotted lines), and the second interface (“gas@IF$_2$”, dashed lines), respectively. The top panels show a smaller range in order to reveal the gas states in more detail. All energies have been shifted with respect to the Fermi level ($E_F$(pure1T/2H)) of the pure 1T/2H MoS$_2$, which was set at 0 eV.](image)

![Figure 7. Projected density of states (PDOS) for NO (left) and NO$_2$ (right) at the position “1T” (on top of the metallic phase). The contributions from the gas molecule and the Mo and S atoms from the 1T and 2H phases are shown as denoted by the legends. All energies have been shifted with respect to the Fermi level ($E_F$(pure1T/2H)) of the pure 1T/2H MoS$_2$, which was set at 0 eV.](image)
is specific for the NO gas molecule. As the gas moves toward the interfaces and the metallic 1T phase, the additional charge provides more electronic states to the material. Because the material at the interfaces and the 1T phase has metallic properties, these states enhance this metallic character by moving toward higher energies and the Fermi level. However, not all states move, so that the strong NO-related peak around $-1.6$ eV remains. This can be based due to the splitting of this main peak. The accuracy of this interpretation remains to be shown. In the end, averaging the peaks over the different gas positions in the figure clearly leads to distinct distributions that could ”read-out” the identities of the gas molecules.

The results on the electronic behavior of the molecule/material system clearly indicate the applicability of the 1T/2H MoS$_2$ 2D material as a probe for gas sensors. In the case of the real sensor, a mixed concentration of gas molecules will be present, revealing a much more complex setup. As it is not possible to model a real device in its full complexity, we provide here additional information with respect to the case where more than one type of gas molecules are present. For this, we have placed at the same time a NO and a O$_2$ molecule at the 2H and the IF$_1$ positions, respectively. The results are provided in the left panel of Figure 9 and clearly reveal distinct electronic peaks for the two gases. Accordingly, also in this simple mixed state, the molecules more or less preserve their characteristic features. Compared to the single 2H phase, due to the hybrid nature of this material, more gas-related states can be sampled as indicated by the variety of the gas-specific electronic states in the eDOS. This can be observed in Figure 9 (right). The peaks from an O$_2$ molecule placed on pure 2H are plotted together with the ones from the same molecule placed on the different positions on top of hybrid 1T/2H MoS$_2$. Note...
that the data are given with respect to the energies of their reference materials. Any conductance should be evaluated as a change in the reference conductance of the pristine materials. These sampled states remain gas specific. It can be easily seen that the pure 2H material provides a higher molecule-specific peak at a certain energy (or gate voltage) compared to the peaks in the case of the hybrid material. However, the advantage of the latter is that measurements can be taken at different gate voltages, increasing the statistics. This is very important in view of a real sensor that should distinguish molecule types within a mixed gas of different concentrations. In such a case, the change in the conductance of the probe material would be of high relevance. This conductance is related to the electronic features of the material. Specifically, the energy peaks in the eDOS can be directly related to the electronic transmission across a device, hence the conductance.\(^\text{17,43}\) Accordingly, the gas specificity found in the eDOS is expected to be mapped onto the conductance of the 2D material. The fact that more molecular states are available compared to the single-phase material indicates a higher gas specificity in the conductance allowing for a better detection of the molecule identity.

## CONCLUSIONS

In this work, we have investigated the potential of a 2D lateral heterostructure made of a metallic MoS\(_2\) ribbon embedded into the semiconducting phase of MoS\(_2\) to detect small gas molecules. To this aim, we have chosen five gas molecules, O\(_2\), CO, CO\(_2\), NO, and NO\(_2\) and placed them at different positions on top of the hybrid 1T/2H MoS\(_2\) material. The positioning was based on our reference study of the preferred adsorption sites and distances of the gas molecules on top of a pure 2H MoS\(_2\). Accordingly, the gas molecules were positioned on top of 1T/2H MoS\(_2\) at certain distances, allowing for a van der Waals type of interaction between molecule and 2D material. For the analysis, we have focused on four distinct positions relating to different phases of the underlying 1T/2H MoS\(_2\). As physically intuitive, different adsorption energies were found for the various molecules. These energies also varied with respect to the positioning of the molecules on top of the material. For example, apart from NO, all other molecules were better adsorbed on one of the interfaces in the material. Overall, the adsorption of the molecules resulted in small modifications of the electronic density of states of the underlying material. These modifications arise from the additional electronic states provided by the gas molecules. Our results clearly show the gas specificity of these peaks, which remains also after the adsorption. This specificity also remains for the various adsorption positions. However, changes in the shape or energy range of the peaks were evident in all cases except the CO gas. Our study could also reveal distinct features between a healthy gas, oxygen, and the poisonous monoxide gases. Most importantly, distinct features in a possible charge transfer were found for the nitrogen oxides revealing the high potential of the 1T/2H MoS\(_2\) material in distinguishing these from other molecules. Such detectable changes could identify large compositions of poisonous gas molecules in air and evaluate the quality of air.

The main aim here was to reveal the high molecule specificity in the electronic properties of the 1T/2H MoS\(_2\) material, thus its sensitivity. Our results cannot directly assess the selectivity of a real gas sensing device. The only reference to selectivity can be made with respect to the different energies at different peaks in the mixed state (see Figure 9). This implies that by swapping a gate voltage in a real device, electronic signals at a different gate could be associated with a certain molecule type. This would give rise to raw gate-dependent electronic current peaks, which could read-out (select) the molecule identity. The gating voltage would in essence tune the measured conductance. In this way, the Fermi level could be selectively shifted in order to capture the desired molecular states found in the eDOS analysis. Depending on the energy range covered, the resulting detectable changes in the conductance would then be assigned to specific gas molecules. In the end, our work strongly points to this possibility. The exact details to achieve this in practice remain to be shown. Further studies should also be extended in including a mixture of different gas molecules and also involve electronic transport calculations. In view of a real sensing device including many sources of noise, the features found here should be enhanced. For this, different strategies such as doping the probe 1T/2H MoS\(_2\) material or combining it with other heterostructures made of other elements could be investigated. These strategies would also improve the charge carrier concentration and the conductivity. Specifically, the exact structure, chemical details, and compositions at the interface of materials can strongly influence the electronic and transport properties of a 2D hybrid material. In this respect, our work on proposing the 1T/2H MoS\(_2\) heterostructure as a possible gas sensor could be used as a first step in tuning materials for sensing applications, not only limited to gas detection.

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### Notes

The authors declare no competing financial interest.

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