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Enhanced Sensitivity of MoSe₂ Monolayer for Gas Adsorption Induced by Electric Field

Wen Ai,¹ Liangzhi Kou,³ Xiaohui Hu,^{*1,2} Yifeng Wang,^{1,2} Arkady V. Krasheninnikov,^{4,5} Litao Sun,⁶ Xiaodong Shen^{1,2}

¹ College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211816, China

² Jiangsu Collaborative Innovation Center for Advanced Inorganic Function Composites, Nanjing Tech University, Nanjing 211816, China

³ School of Chemistry, Physics and Mechanical Engineering Faculty, Queensland University of Technology, Garden Point Campus, Brisbane, QLD 4001, Australia

⁴ Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany

⁵ Department of Applied Physics, Aalto University School of Science, PO Box 11100, 00076 Aalto, Finland

⁶ SEU-FEI Nano-Pico Center, Key Laboratory of MEMS of Ministry of Education, Collaborative Innovation Center for Micro/Nano Fabrication, Device and System, Southeast University, Nanjing 210096, China

Corresponding Author: xiaohui.hu@njtech.edu.cn (XH)

Abstract

According to recent studies, gas sensors based on MoSe₂ have better detection performance than graphene-based sensors, especially for N-based gas molecules, but the reason for that is not fully understood at the microscopic level. Here, we investigate the adsorption of CO, CO₂, NH₃, NO and NO₂ gas molecules on MoSe₂ monolayer by the density functional theory calculations. Our results reveal that indeed MoSe₂ monolayer is more sensitive to adsorption of N-containing gas molecules than C-containing, which can be attributed to the distinct charge transfer between the gas molecules and MoSe₂. The conductance was further calculated using the nonequilibrium Green's function (NEGF) formalism. The reduced conductance was found for NH₃ and NO₂ adsorbed MoSe₂, consistent with the high sensitivity of MoSe₂ for NH₃ and NO₂ molecules in the recent experiments. In addition, the adsorption sensitivity can significantly be improved by an external electric field, which implies the controllable gas detection by MoSe₂. The magnetic moments of adsorbed NO and NO₂ molecules can also be effectively modulated by the field-sensitive charge transfer. Our results not only give microscopic explanations to the recent experiments, but also suggest using MoSe₂ as a promising material for controlled gas sensing.

Keywords: transition metal dichalcogenides, gas sensor, density functional theory calculations, electric field

Introduction

Two-dimensional (2D) nanomaterials are ideal platforms for building nanoscale sensors due to their reduced dimensionality and excellent properties [1-8]. Recently,

2D transition metal dichalcogenides (TMDs) have attracted great interest as chemical sensors owing to their high carrier mobility [9-14], large surface-to-volume ratio [15-21], and rapid electrical response to the changes in the environments [22-24]. For instance, monolayer and multi-layer MoS₂ films have been found to be extremely sensitive to the environmental gas molecules, especially to NO, NO₂ and NH₃ [25-27]. MoSe₂ layer, one of the most important materials in the family of 2D TMDs, is expected to have excellent sensing performance due to similar electronic properties, and also the fact that the phototransistors based on MoSe₂ exhibited outstanding responsivity, high specific detectivity and fast response time [28, 29]. Indeed, recent experimental studies demonstrated that MoSe₂ sheets possess a competitive advantage over traditional graphene sensors [30]. In addition, Late *et al.* reported high-performance MoSe₂-based NH₃ gas sensors with a detection limit down to 50 ppm [31]. More recently, a multilayer MoSe₂ gas sensor has exhibited ultra-high sensitivity ($S \sim 2 \times 10^3$ for NO₂ at 300 ppm), owing to changes of the gap states near the valence band induced by the NO₂ adsorption [32]. However, the formation of these gap states has not been explained, and further verification is desired to carry out. These reports have stimulated exploration of MoSe₂ as a prospective sensing material.

In fact, the adsorption performance is mainly based on the charge transfer between the adsorption substrate and the gas molecules, which plays an important role in determining the performance of gas sensors. Therefore, effective control for electron transfer between gas molecules and sensing materials can modulate the sensitivity.

Calculations have demonstrated that the sensing properties of low dimensional materials, such as carbon nanotubes [33, 34], graphene [35, 36] and MoS₂ [37], are controllable by external electric field. For example, recent studies indicated that the adsorption of NO₂ based on Ga-doped graphene was effectively enhanced by the electric field, as manifested by the increase in adsorption energy [36]. Moreover, the charge transfer between the adsorbed molecule and MoS₂ can also be controlled by the external electric field [37]. In addition, the applied electric field could significantly enhance the CO gas sensitivity of the antimonene [38], which is beneficial for the application of CO gas sensor at room temperature. These studies suggested that the external electric field can dramatically change the affinity and electronic properties of the adsorption system. Therefore, it is expected that the electric field can effectively modulate the charge transfer between gas molecules and MoSe₂, which inspired us to study if sensitivity of MoSe₂ for gas sensors can be improved by applying external electric field.

In this work, by means of systematic density functional theory (DFT) calculations, we examine the most stable adsorption configurations and also evaluate adsorption energy, charge transfer, and magnetic properties of gas molecules (CO, CO₂, NH₃, NO and NO₂) on MoSe₂ monolayer. The results show that the adsorption energies of N-based gas molecules are larger than those for CO and CO₂ adsorption, which is related to the distinct charge transfer between the gas molecules and MoSe₂. The reduced conductance was found for NH₃, NO and NO₂ adsorbed MoSe₂, which well explains

the high sensitivity of MoSe₂ to NH₃ and NO₂ adsorption as seen in recent experiments. In addition, the adsorption sensitivity can be significantly improved by an external electric field. The magnetic moments of adsorbed NO and NO₂ molecules can effectively be modulated by the charge transfer, which is sensitive to the applied electric field. Our results not only explain the recent experiments [31] at the atomistic level, but also suggest using MoSe₂ as a superior gas sensor.

Calculation details

Our calculations were carried out using the VASP package [39, 40] based on DFT. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used for the exchange and correlation interactions [41]. The projector-augmented-wave (PAW) method was employed to describe electron-ion interactions [42, 43]. Van der Waals corrections were included through Grimme's DFT-D2 method as implemented in VASP [44, 45]. The plane wave cutoff energy was set to 500 eV, because a higher value had little effect on the results. The structures were relaxed until the energy and the force on each atom were less than 10^{-5} eV and 0.01 eV/Å, respectively. A k-point sampling of $9 \times 9 \times 1$ and $19 \times 19 \times 1$ were used for the structural relaxations and self-consistent calculations. The vacuum region of 15 Å was introduced to avoid interaction between periodic images of slabs. The charge transfer between gas molecules and MoSe₂ was calculated using Bader analysis [46]. Spin polarization was included in the calculations of the adsorption of paramagnetic molecules NO and NO₂. The electronic transport properties were studied by the NEGF

method implemented in the TRANSIESTA package [47].

Results and discussion

To model the absorption of CO, CO₂, NH₃, NO and NO₂ molecules on the surface of MoSe₂ monolayer, a 4 × 4 supercell of MoSe₂ was chosen. The optimized lattice constant of MoSe₂ monolayer was found to be 3.32 Å, consistent with the previous results [48,49]. In order to obtain the most stable adsorption configuration, the four different adsorption sites were considered (see Figure S1 in Supporting Information). (i) H site (on the top of a hexagon center), (ii) Tm (on the top of a Mo atom), (iii) Ts (on the top of a Se atom), (iv) B site (on the top of a Mo-Se bond). The top and side views of the most favorable configurations for CO, CO₂, NH₃, NO and NO₂ adsorbed on MoSe₂ are shown in Figure 1. For the CO and CO₂ molecules, the C atom is located at the Tm and Ts sites. The adsorption distance between the CO molecule and MoSe₂ (2.94 Å) is smaller than the value for CO₂ adsorption (3.30 Å). However, NH₃ and NO₂ molecules are located at the H site. The distances for NH₃ and NO₂ adsorption are 2.72 Å and 2.77 Å, respectively. In contrast, for NO, the molecule moves to the B site with the adsorption distance of 2.88 Å, as shown in Figure 2(a). The values indicate that upon adsorption the N-based gas molecules have the smaller distance as compared to those for CO and CO₂ molecules.

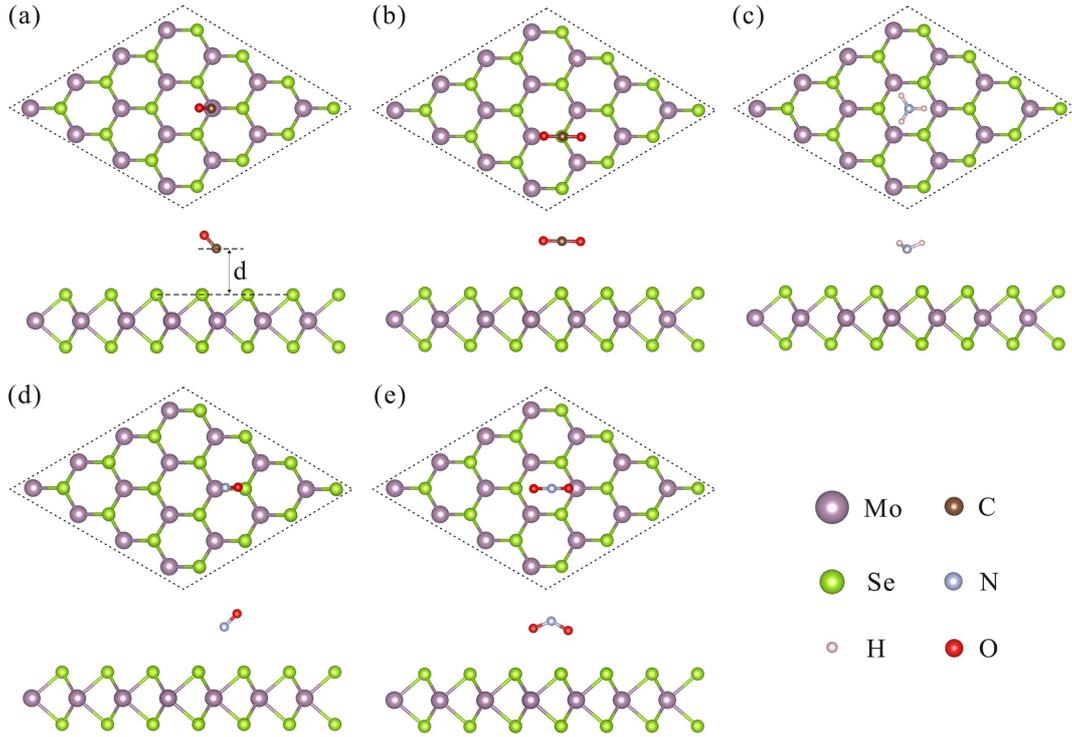


Figure 1. Top and side views of (a-e) the most favorable configurations of (a) CO, (b) CO₂, (c) NH₃, (d) NO, and (e) NO₂ adsorbed on MoSe₂ monolayer. The definition for the adsorption distance d is given in (a).

In order to get a quantitative description of the adsorption strength on MoSe₂ monolayer for different gas molecules, the adsorption energy was computed. The adsorption energy is defined as $E_a = E_{\text{MoSe}_2} + E_{\text{molecule}} - E_{\text{total}}$, where E_{total} is the total energy of MoSe₂ with an adsorbed molecule, E_{MoSe_2} and E_{molecule} are the total energies of the pristine MoSe₂ and isolated molecule, respectively. According to this definition, a more positive E_a value indicates a stronger adsorption. The calculated values of adsorption energy are displayed in Figure 2b. It is found that CO has the minimum adsorption energy of 0.099 eV, while NO₂ has the maximum adsorption energy of 0.199 eV. The adsorption energies of CO₂, NO, and NH₃ are 0.144, 0.167,

and 0.187eV, respectively. The results show that the adsorption energies of N-based gases are larger than those for CO and CO₂ adsorption, which well correlates with the adsorption distances presented in Figure 2a. This indicates that MoSe₂ is more sensitive to adsorption of N-based gases, which is similar to MoS₂ and graphene that are sensitive to adsorption of N-based gases [14,26]. Among them, NH₃ and NO₂ have the highest adsorption energy, which explains the higher sensitivity to NH₃ and NO₂ adsorption on MoSe₂ as seen in the recent experiments [31, 32].

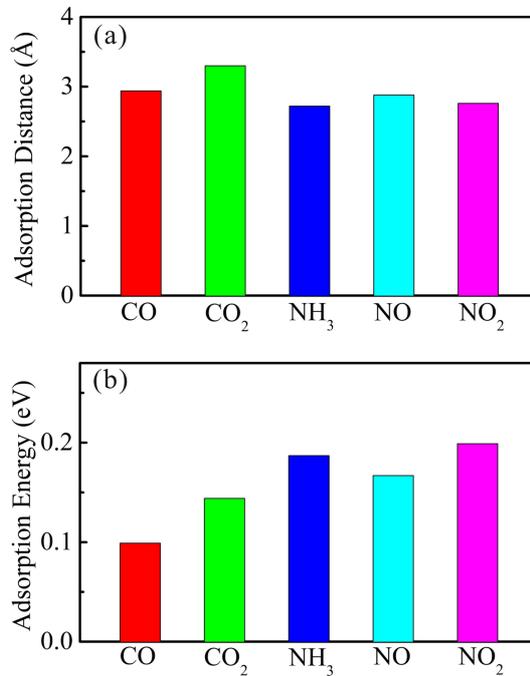


Figure 2. (a) Distance between the gas molecule and the MoSe₂ monolayer, defined as in Figure 1a. (b) Adsorption energy for CO, CO₂, NH₃, NO, and NO₂ on MoSe₂ monolayer.

Previous studies indicate that charge transfer plays an important role in the adsorption strength and the decrease in the resistance of MoS₂ [50]. Thus, we calculated the charge difference between the gas molecules and MoSe₂ monolayer (Figure 3), which is defined as $\Delta\rho = \rho_{\text{gas/MoSe}_2} - \rho_{\text{gas}} - \rho_{\text{MoSe}_2}$, where $\rho_{\text{gas/MoSe}_2}$, ρ_{gas} and

ρ_{MoSe_2} represent the charge density of the gas molecules adsorption system, the isolated gas molecule and the free MoSe₂ monolayer, respectively. Both the gas molecule and free MoSe₂ have the same coordination as that in the adsorbed configuration. To have a quantitative picture, Bader analysis was performed to extract the charge transfer amount induced by the gas adsorption. As shown in Figure 3a and 3b, for CO and CO₂ adsorption, the small amount of charge transfer (0.015 e and 0.025 e, respectively) is observed from MoSe₂ monolayer to the gas molecules, indicating the weak binding. However, for N-based gas molecules, larger charge transfer takes place, suggesting a stronger binding between the gas molecules and MoSe₂ monolayer. Especially for NO₂, up to 0.149 e is transferred from MoSe₂ monolayer to the molecule (Figure 3e), which has the strongest binding. For NH₃ and NO adsorption in Figure 3c and d, the charge transfer (0.029 e and 0.035 e, respectively) is smaller than that for NO₂, but still larger than those for CO and CO₂. The comparison of the amount of the charge transfer and the adsorption energy (strength) presented in Figure 2b shows a clear correlation, which can help us to understand the mechanism for gas molecule adsorption on MoSe₂ monolayer. In addition, it is evident from Figure 3 that most molecules (such as CO, CO₂, NO and NO₂) are charge acceptors, whereas NH₃ behaves as a charge donor. The phenomenon is similar to the cases of gas adsorption on graphene and MoS₂ [37,51], where the gas molecules also behave as either charge acceptors or donors. For the n-type MoSe₂, some electrons have already existed in the conduction band. Upon CO, CO₂, NO and NO₂ adsorption, electron charge is transferred to the gas molecules from

MoSe₂, leading to an increased resistance and decreased current of MoSe₂. Then, the mechanism of the MoSe₂-FET gas sensor for NO₂ can be understood [32].

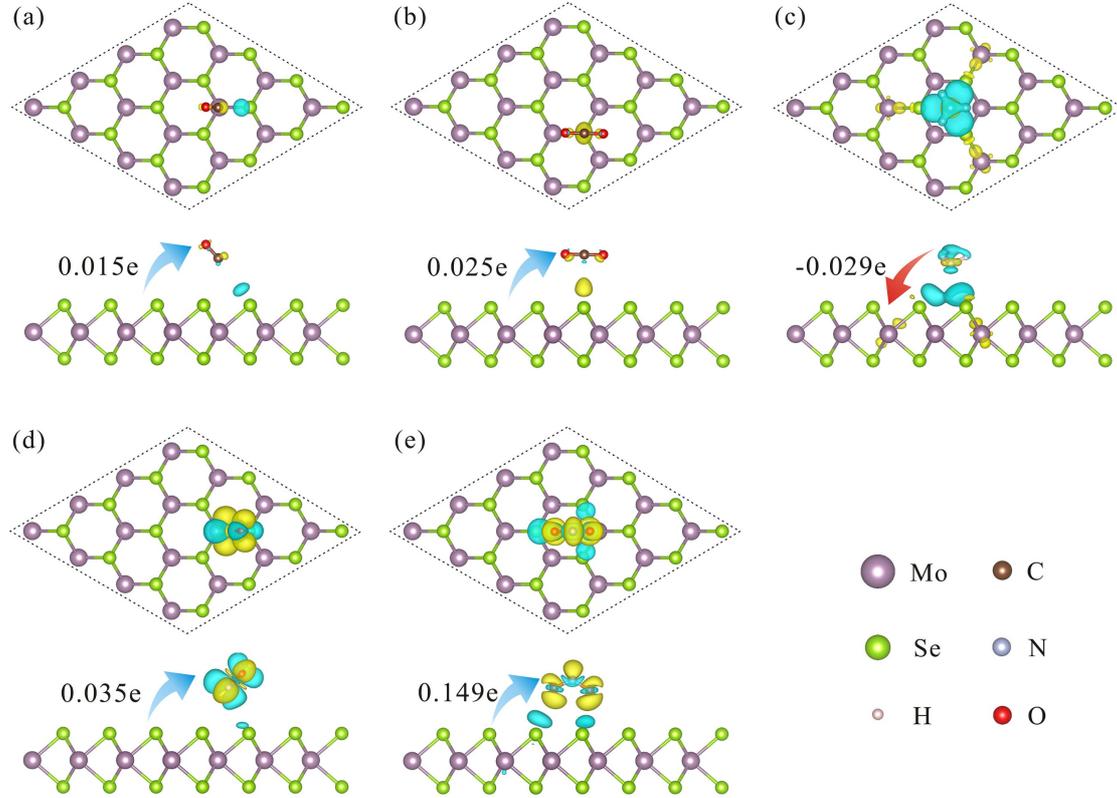


Figure 3. The charge difference between MoSe₂ monolayer and gas molecules for (a) CO, (b) CO₂, (c) NH₃, (d) NO and (e) NO₂. The isosurface is taken at $6.0 \times 10^{-4} \text{ e}/\text{\AA}^3$. The electron accumulation (depletion) is indicated by yellow (blue) color. The direction (indicated by an arrow) and value of the charge transfer are shown.

Next, we examine the effects of gas adsorption on the electronic properties of MoSe₂ monolayer. Figure 4a shows the band structure of MoSe₂ monolayer, which has a direct bandgap of 1.44 eV, in accordance with previous reported results [48,49]. Figure 4b-d present the band structure of MoSe₂ monolayer with the adsorption of CO, CO₂ and NH₃, as well as the projected band structure from the gas molecules. It is found that upon CO, CO₂ and NH₃ adsorption, neither the valence bands nor conduction band of

MoSe₂ monolayer is significantly influenced, as the impurity states induced by gas molecules located away from the Fermi level. Thus, CO, CO₂ and NH₃ adsorption does not modify the band structure near the Fermi level, and has no substantial influence on the electronic structure of MoSe₂ monolayer. On the other hand, the spin-polarized band structure of NO and NO₂ adsorbed MoSe₂ is displayed in Figure 4e and f. It is seen that for paramagnetic NO and NO₂ adsorption, some flat impurity states are clearly observed in the band gap of the host MoSe₂ monolayer. Specifically, NO introduces two spin-up states at -0.12, 0.12 eV and one spin-down state at 0.55 eV close to the Fermi level in the band gap (see Figure 4e). NO₂ introduces one spin-down state at 0.14 eV above the Fermi level in the band gap, given in Figure 4f. Our findings clearly explain the origin of the gap states in NO₂ adsorbed MoSe₂ in the recent experiments [32].

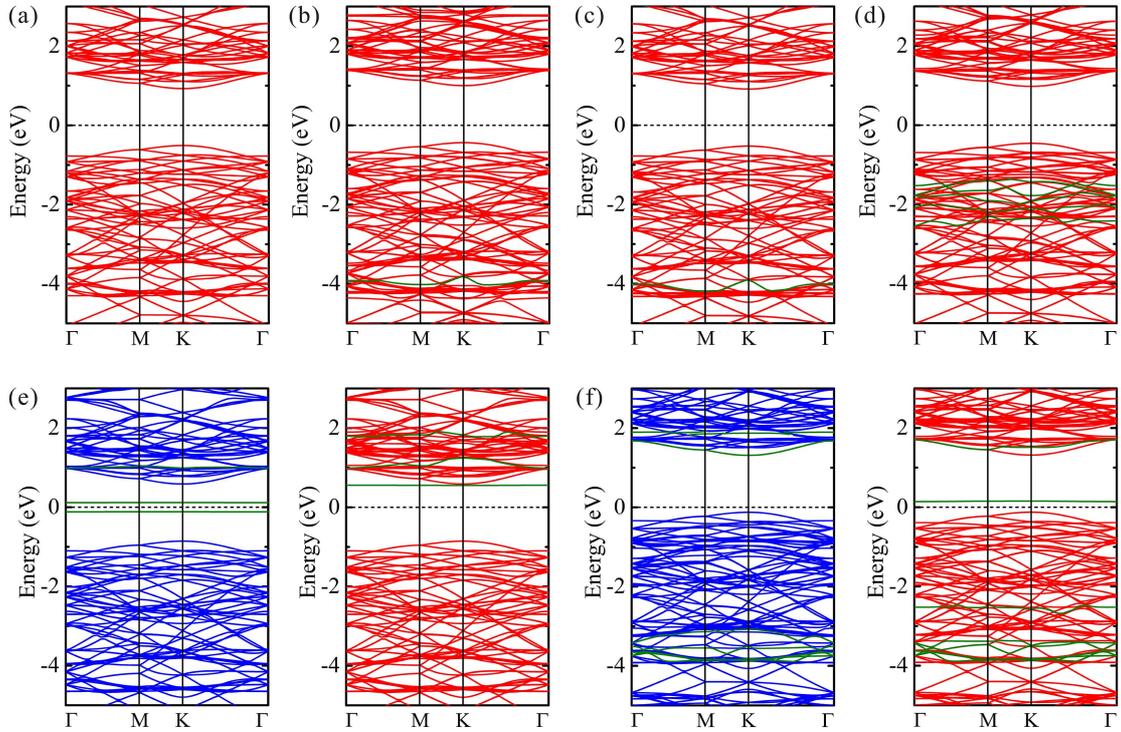


Figure 4. (a) The band structure of pristine MoSe₂. Band structure of (b) CO, (c) CO₂, (d) NH₃, (e) NO and (f) NO₂ adsorbed on MoSe₂ monolayer. The blue and red lines denote spin-up and spin-

down channels, respectively. The olive lines represent the projected band structure of the adsorbed gas molecules.

To further analyze the changes in electronic structure of MoSe₂ upon adsorption of the gas molecules, the projected density of states (PDOS) are calculated and presented in Figure 5. In the pristine MoSe₂ monolayer, the conduction band minimum is mainly described by Mo d_z² orbitals, while the valence band maximum is mostly contributed from Mo d_{xy} and d_x² orbitals [48, 49]. For the CO and CO₂ adsorption, we did not observe noticeable changes around the Fermi level upon adsorption of the molecules, as indicated in Figure 5b and c, which is consistent with their small adsorption energies. Meanwhile, the adsorption of the NH₃ molecule induces some impurity states in the energy range around -2 eV, which leads to the hybridization of the N p_z orbital with the d_z², d_x² and d_{xy} orbitals of the Mo atom. Overall, the adsorption of CO, CO₂ and NH₃ molecules does not have a noticeable effect on the DOS near the Fermi level. For the adsorption of NO, it can be seen from Figure 5e that the NO p_y and p_z orbitals dominate two DOS peaks around the Fermi level, which results in the flat impurity states for the spin-up electrons (see Figure 4e). Similarly, the adsorption of NO₂ produces a spin-down impurity state near the Fermi level, which is mainly composed of O p_z orbitals, as shown in Figure 5f. It can be concluded that the adsorption of paramagnetic molecules NO and NO₂ induces the impurity states around the Fermi level, which have the obvious influence on the electronic structure of MoSe₂, as manifested in their higher adsorption energy.

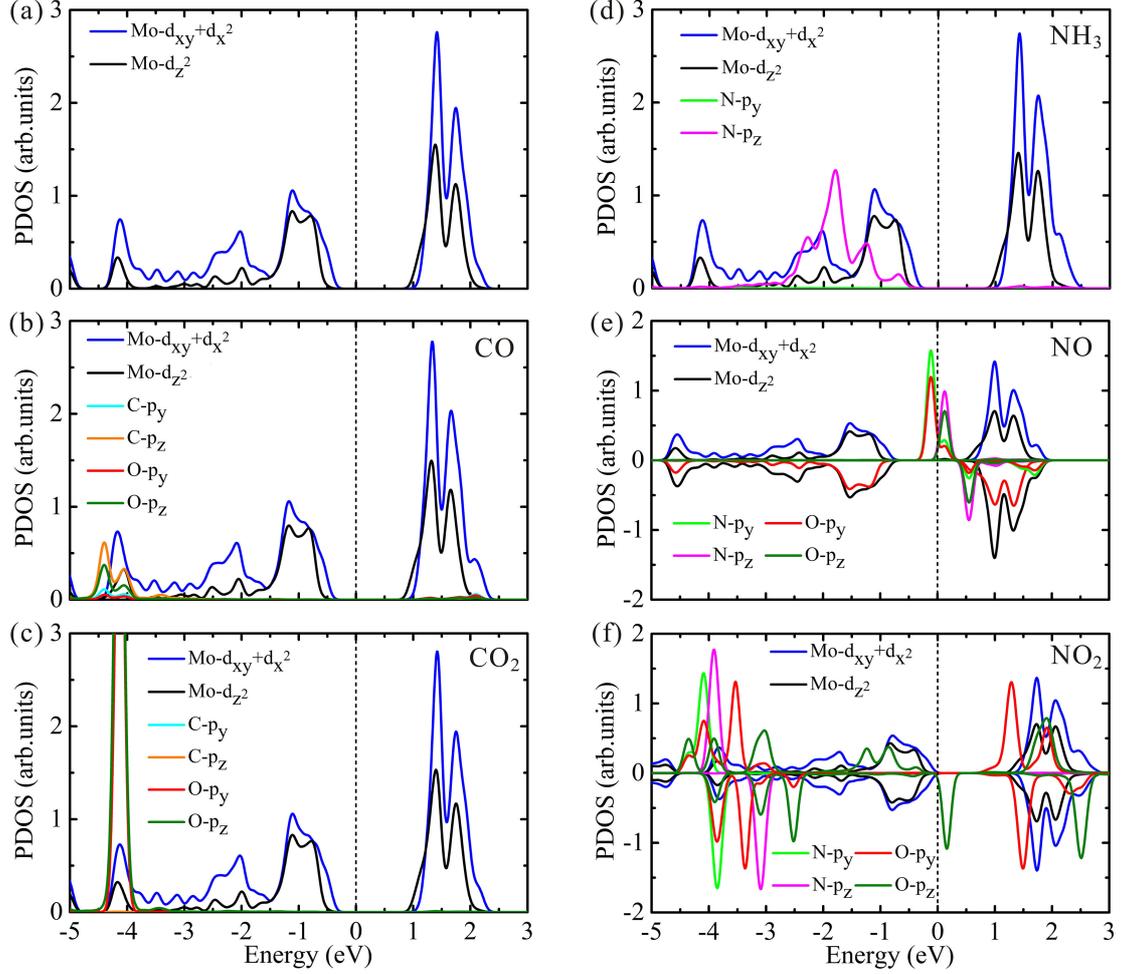


Figure 5. (a) PDOS of pristine MoSe₂. PDOS of (b) CO, (c) CO₂, (d) NH₃, (e) NO and (f) NO₂ adsorbed on MoSe₂ monolayer.

Although the electronic properties of MoSe₂ are not significantly influenced by CO, CO₂, and NH₃ adsorption, the resistivity of the system can be directly measured experimentally, which can be used as a signal for detecting gas molecules. In order to explore the resistivity change, we carried out the calculation of the conductance for MoSe₂ before and after the gas adsorption by the NEGF method. A two-probe system, where semi-infinite left and right electrode regions are in contact with the central scattering region, is used to calculate the electron transport properties, as shown in Figure 6a. We chose a 4×4 supercell without gas adsorption for each of the left and

right electrodes, whereas the center scattering region was represented by a 4×4 supercell with adsorbed gas molecules. Calculations for a 4×4 central scattering region without gas adsorption were also done for comparison. For the nonmagnetic gas molecules adsorption (CO_2), the conductance of the system was almost unchanged as compared to the pristine MoSe_2 , while for CO and NH_3 the conductance was detectably reduced, as shown in Figure 6b. The smaller conductance means a reduced current, which can be directly used to compare with the experimental measurements. Similarly, a reduction in the conductance for NO and NO_2 adsorbed MoSe_2 is also observed, Figure 6c, indicating the high sensitivity of MoSe_2 sensor to N-based gas molecules. It should be noted that the significantly decreased conductance of MoSe_2 with adsorbed NH_3 and NO_2 molecules is consistent with the high sensitivity of MoSe_2 for NH_3 and NO_2 molecules reported in the recent experiments [31, 32].

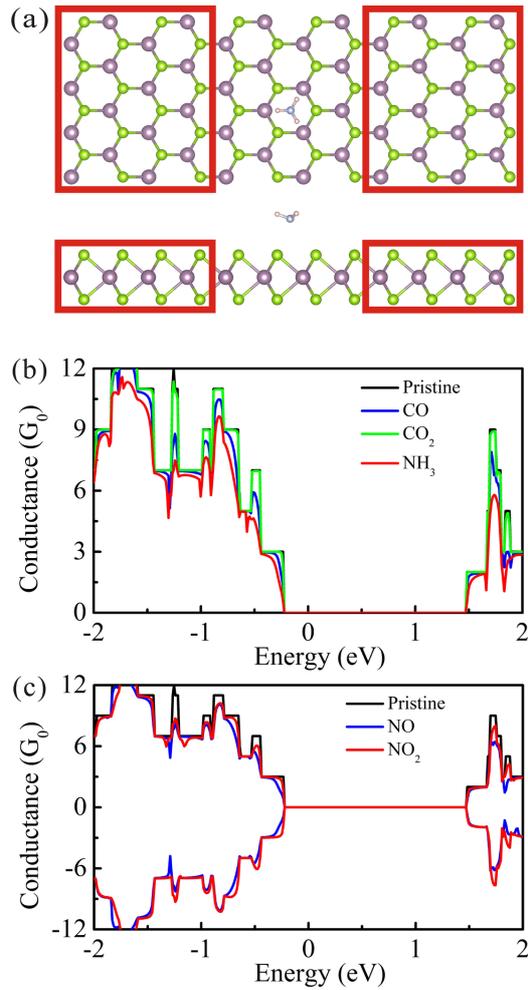


Figure 6. (a) Illustration of the two-probe systems where semi-infinite left and right electrode regions (red square region) are in contact with the central scattering region. The conductance of pristine MoSe₂ monolayer before and after (b) CO, CO₂ and NH₃, (c) NO, NO₂ gas molecules adsorption.

Previous studies showed that the charge transfer upon adsorption can be tuned by perpendicular electric field, which plays an important role in determining the performance of MoSe₂ sensor. To explore the effect of the electric field on charge transfer, we applied an external vertical electric field across the plane of MoSe₂ monolayer. The positive direction of the electric field is defined from MoSe₂ monolayer to gas molecules. Taking the paramagnetic NO and NO₂ molecules as the representative

systems, we investigated the relationship between applied electric field with charge transfer, adsorption energy, adsorption distance as well as magnetic moment, displayed in Figure 7. It can be seen from Figure 7a that the adsorption energy is sensitive to the applied electric field. Along a positive electric field, the adsorption energy consistently increases with the increasing electric field. When a negative electric field is applied, the adsorption energy gradually decreases with the increasing negative electric field. In general, higher adsorption energy implies higher sensitivity for sensing application. The adsorption energy variation can be understood from the corresponding charge transfer and the adsorption distance, displayed in Figure 7b and c. Due to the strong electronegativity of N and O atoms, NO and NO₂ molecules are negatively charged. As compared to the case without electric field, there is additional electron transferred from MoSe₂ to NO and NO₂ at $E = 1 \text{ V/\AA}$, which will enhance the backdonation effect, as manifested in the enhanced adsorption energy and the reduced adsorption distance. On the other hand, the electrons transfer from NO and NO₂ to MoSe₂ as the increasing negative electric field, which weakens the backdonation effect and leads to smaller adsorption energy and larger adsorption distance. The same trend in the adsorption energy with charge transfer in the presence of the electric field was found upon adsorption of gas molecules on Ga-doped graphene [36]. Our results suggest that the sensitivity of MoSe₂ with adsorbed NO and NO₂ molecules can be significantly improved by applying an external vertical electric field.

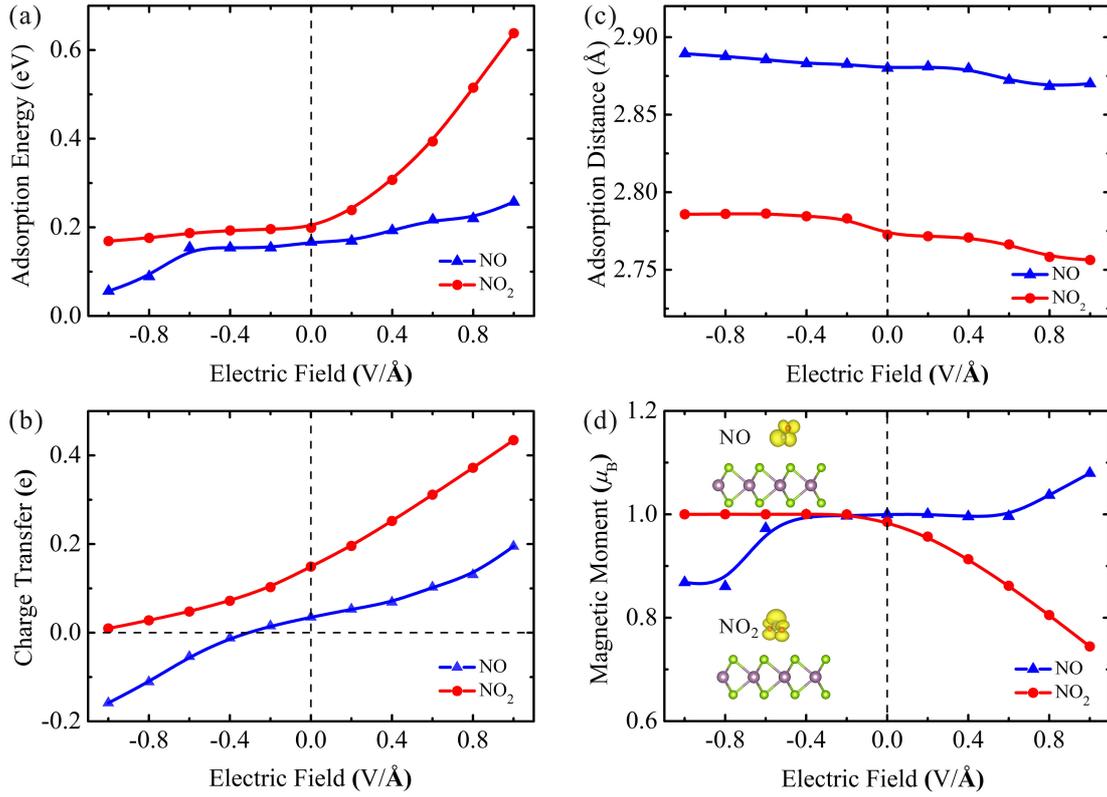


Figure 7. Variation of (a) the adsorption energy, (b) the charge transfer, (c) the adsorption distance and (d) the magnetic moment as a function of electric field strength for NO and NO₂ adsorbed on MoSe₂ monolayer. The insets show the spatial spin density distribution on NO and NO₂ molecules.

At the same time, the adsorption of NO and NO₂ molecules can induce a magnetic moment of $1.0 \mu_B$ and $0.99 \mu_B$, respectively. The spin density distribution shown in Figure 7d indicates that the spin-polarized electrons are mainly located on the NO and NO₂ molecules. Interestingly, the magnetic moment can be tuned by the applied electric field, as shown in Figure 7d. As for NO adsorption, the magnetic moment is almost unchanged in the low electric field strength. However, the magnetic moment reaches $1.08 \mu_B$ or reduces to $0.87 \mu_B$ at the electric field $E = 1 \text{ V/\AA}$ and -1 V/\AA , which can be attributed to the charge transfer. A Bader analysis indicates that there is 0.035 e electron transferred to NO at the absence of electric field, while NO accepts 0.195 e and donates

0.159 μ_B at $E = 1 \text{ V/\AA}$ and -1 V/\AA , respectively. Similarly, for NO_2 adsorption, the magnetic moment does not change too much due to charge transfer under a negative electric field, while it decreases to $0.74 \mu_B$ at $E = 1 \text{ V/\AA}$. Thus, the magnetic moment of NO and NO_2 gas molecules on MoSe_2 can be effectively modulated by applying an external vertical electric field, which provides new strategy for constructing MoSe_2 -based spin devices.

Conclusions

In summary, using systematic DFT calculations, we have investigated the adsorption energy, charge transfer, electronic and magnetic properties of the gas molecules (CO , CO_2 , NH_3 , NO and NO_2) adsorbed on MoSe_2 monolayer. The results show that the adsorption energies of N-based gas molecules are larger than those for CO and CO_2 molecules, suggesting that MoSe_2 is more sensitive to N-based gas molecules. Particularly, NO_2 adsorption has the highest adsorption energy, which can help us to understand the mechanism of the MoSe_2 -FET gas sensor operation upon NO_2 adsorption. The reduced conductance was found for NH_3 , NO and NO_2 adsorbed MoSe_2 , consistent with the high sensitivity of MoSe_2 for NH_3 and NO_2 molecules as seen in the recent experiment. In addition, the adsorption sensitivity can be significantly improved by an external electric field. The magnetic moment of adsorbed NO and NO_2 molecules can effectively be modulated by the charge transfer, which is sensitive to the applied electric field. Our results not only explain the recent experiments, but also suggest using MoSe_2 as a superior gas sensor.

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