Abstract: The SF$_6$/N$_2$ gas mixture is an alternative gas to SF$_6$. SF$_6$/N$_2$ will decompose and generate nitrogenous characteristic gases, such as NO, NO$_2$, N$_2$O, and NF$_3$, when exposed to long-term partial discharge. The adsorption models of Ti$_3$C$_2$T$_x$ (T=O, F, OH) and NO, NO$_2$, N$_2$O, NF$_3$ were constructed, and the most stable adsorption structure was selected in this paper. The electron density and density of states of the adsorption system were further analyzed to study the adsorption behavior, and the sensing performance was evaluated in the end. The results are as follows: four gases could be spontaneously adsorbed on Ti$_3$C$_2$T$_x$, and strong adsorption occurred when surface terminal groups were OH, forming hydrogen or chemical bonds with significant charge transfer. Results show that Ti$_3$C$_2$(OH)$_2$ had a stronger sensing ability than Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$O$_2$. The conductivity of the Ti$_3$C$_2$T$_x$ with different terminal groups was improved after the adsorption of NO and NO$_2$, showing Ti$_3$C$_2$T$_x$ had a good sensing ability for NO and NO$_2$. It was difficult for the four gases to desorb from the Ti$_3$C$_2$(OH)$_2$ surface, but the adsorption on the Ti$_3$C$_2$F$_2$, Ti$_3$C$_2$O$_2$ surface had a short recovery time at room temperature.

Keywords: Ti$_3$C$_2$T$_x$; SF$_6$/N$_2$ decomposition characteristic products; gas sensor; DFT

1. Introduction

SF$_6$ has been widely used in high-voltage electrical equipment because of its excellent insulation and arc extinguishing properties. However, SF$_6$ is a greenhouse gas, and its global warming potential is 23,900 times that of CO$_2$, and it can exist in the atmosphere for more than 3200 years. It is one of the six greenhouse gases prohibited by the Kyoto Protocol [1–3]. In order to relieve the environmental pressure brought about by SF$_6$, the power industry has used the SF$_6$/N$_2$ gas mixture as an insulation medium. SF$_6$/N$_2$ not only has good insulation performance but also solves the problem of high SF$_6$ liquefaction temperature. It can effectively reduce the use and emission of SF$_6$ and relieve the greenhouse effect of SF$_6$ [4–6].

In the long-term running of power equipment, various insulation defects will unavoidably occur, and insulation faults, such as partial discharge or overheating, will be generated under the combined action of voltage and current. SF$_6$/N$_2$ will gradually decompose under the continuous action of these faults, generating not only sulfur-containing characteristic gases, such as SO$_2$, SOF$_2$, SO$_2$F$_2$, and H$_2$S [7], but also nitrogen-containing characteristic gases, such as NO, NO$_2$, N$_2$O, and NF$_3$ [8–10]. Since the SF$_6$/N$_2$ fault decomposition process is directly related to the fault properties, the internal insulation fault of the equipment...
can be detected in time by monitoring fault decomposition characteristic products, which is essential for the safe operation of gas-insulated equipment [11,12].

Two-dimensional layered nanomaterials have excellent electrical, mechanical, and optical properties due to their unique structure, and their high specific surface area is conducive to gas adsorption and sensing [13–17]. Two-dimensional transition metal carbides, carbon and nitrogen compounds (collectively called MXene) have received a lot of attention and research from researchers since their discovery in 2011. MXene has the chemical formula M_{n+1}X_nT_x (n = 1–3), where M represents the transition metal (such as Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, etc.), X is carbon or nitrogen, and T_x stands for terminal group, such as fluorine, oxygen, or hydroxyl. Ti$_3$C$_2$T$_x$ was the first MXene synthesized and has been used in many sensing-related studies.

Eunji Lee et al. [18] prepared a sensor of Ti$_3$C$_2$T$_x$ and successfully detected all the tested volatile organic compound gases at room temperature. Then, they proposed a possible sensing mechanism for the sensor by analyzing the interaction between the gas and the majority carrier of the material. Chen et al. [19] chose Ti$_3$C$_2$T$_x$ and WSe$_2$ as materials for hybridization and prepared the Ti$_3$C$_2$T$_x$/WSe$_2$ hybrid sensor with low noise level and ultra-fast response and recovery time. It has high sensitivity and selectivity for detecting oxygenated volatile organic compounds. Wu et al. [20] realized the detection of NH$_3$ by Ti$_3$C$_2$T$_x$ at room temperature and investigated its highly selective adsorption behavior using the density functional theory (DFT) calculations. Kong et al. [21] adsorbed SF$_6$ decomposition gas on Ti$_3$C$_2$T$_x$ using Quantum Espresso software and modified the surface of Ti$_3$C$_2$T$_x$ by adding atomic vacancies. The results showed that Ti$_3$C$_2$T$_x$ with dot vacancies can detect SF$_6$ decomposition products with high sensitivity and low electronic noise, and the sensitive detection ability for SO$_2$ is especially obvious.

Based on the previous research on gas-sensitive sensing of Ti$_3$C$_2$T$_x$ for sulfur-containing gases [22], this paper performed first-principle calculations on the adsorption behavior of SF$_6$/N$_2$ nitrogen-containing fault decomposition characteristic components on the surface of Ti$_3$C$_2$T$_x$ with different terminal groups, and adsorption morphology, adsorption distance, adsorption energy, charge transfer, electron density, and density of states were analyzed to explore the gas sensing ability of Ti$_3$C$_2$T$_x$ with different terminal groups for NO, NO$_2$, N$_2$O, and NF$_3$.

2. Computational Methods

This paper is mainly based on the DFT. The simulation calculations regarding the adsorption system of gas molecules with Ti$_3$C$_2$T$_x$ are carried out in the DMol$^3$ module of Material Studio [23]. In this paper, a 3 × 3 × 1 periodic supercell of Ti$_3$C$_2$T$_x$ is established. Firstly, NO, NO$_2$, N$_2$O, and NF$_3$ gases are placed on the surface of Ti$_3$C$_2$T$_x$, and multiple directions and different possible sites of gas molecules adsorption are considered. Then, the most stable adsorption site of gas molecules is finally selected for further analysis according to the energy of the system. The K-point settings of the Brillouin zone for structure optimization and electronic property calculation are $4 \times 4 \times 1$ and $8 \times 8 \times 1$, respectively, and the optimization of the structure, energy, and related properties of the gas–solid interface system are calculated by the GGA-PBE method [24,25]. The DNP basis group is chosen for the expansion of the electronic wave function [26], and the Grimme method in the DFT-D dispersion correction is used to describe the van der Waals interaction forces [27,28]. For the paramagnetic molecules NO, NO$_2$, and N$_2$O, the computational setup takes into account the spin polarization [29]. The all-electron model is used for the core treatment of the gas molecules, and the DFT Semi-core pseudopotential (DSSP for short) is used for the solid surface. The energy convergence threshold, the maximum force threshold, and the maximum displacement threshold for geometric optimization are set to $2.0 \times 10^{-3}$ Ha, 0.004 Ha/Å, and 0.005 Å, respectively, and the convergence accuracy of SCF is $1.0 \times 10^{-5}$. The direct inversion DIIS value in the SCF iterative subspace is set to 6, and the smearing value of the thermal tailing effect is set to 0.005 Ha. In addition, to eliminate the interaction of adjacent layers, a 25 Å vacuum layer is set in the z-direction. The strength
of the interaction between the gas molecules and the sensing material is expressed by the adsorption energy \( (E_{\text{ads}}) \) as follows:

\[
E_{\text{ads}} = E_{\text{total}} - E_{\text{gas}} - E_{\text{substrate}}
\]

where \( E_{\text{total}} \), \( E_{\text{gas}} \), and \( E_{\text{substrate}} \) represent the total energy of the gas/Ti\(_3\)C\(_2\)T\(_x\) adsorption system, isolated gas molecule, and pristine Ti\(_3\)C\(_2\)T\(_x\), respectively.

\( Q_t \) represents the charge transfer between the gas molecule and Ti\(_3\)C\(_2\)T\(_x\) during the adsorption as follows:

\[
Q_t = Q_1 - Q_2
\]

where \( Q_1 \) and \( Q_2 \) represent the total charges of the adsorbed and the isolated gas molecules. A negative value of \( Q_t \) means the electrons’ transfer from the substrate to gas molecules.

3. Results and Discussion

3.1. Gas Adsorption on Ti\(_3\)C\(_2\)F\(_2\)

When gas molecules make contact with Ti\(_3\)C\(_2\)F\(_2\) surface, adsorption may occur at different sites. The most stable adsorption sites of gas molecules and the orientation of adsorption on Ti\(_3\)C\(_2\)F\(_2\) were selected according to the value of adsorption energy, as shown in Figure 1, where Figure 1a–h show the top and side views of the gas after adsorption. The structure after adsorption shows that no significant changes occur in the gases as well as the substrate material during the adsorption process. The adsorption distances of gas molecules with Ti\(_3\)C\(_2\)F\(_2\) are all between 2.8 Å and 3.0 Å, as shown in Table 1. After measurement and comparison, the bond length of the adsorbed gas molecules does not change significantly, and the specific values of the bond length change are shown in Table 1 (The original bond lengths of the four gas molecules are shown in Figure S1). Table 2 gives the adsorption energies of the four gas molecules on the best adsorption sites of Ti\(_3\)C\(_2\)F\(_2\), and the adsorption energies of NO, NO\(_2\), N\(_2\)O, and NF\(_3\) are \(-0.216 \text{ eV}\), \(-0.213 \text{ eV}\), \(-0.273 \text{ eV}\), and \(-0.323 \text{ eV}\), respectively. The negative adsorption energies indicate that the adsorption of gases does not require external energy.

### Table 1. Adsorption distance and bond length change of gas molecules on Ti\(_3\)C\(_2\)T\(_x\).

| Ti\(_3\)C\(_2\)T\(_x\) | Gas  | D(Å) \(^a\) | L(Å) \(^b\) |
|----------------------|------|------------|-----------|
| F                    | NO   | 2.978      | -0.012    |
|                      | NO\(_2\) | 2.807      | 0.011     |
|                      | N\(_2\)O | 2.979      | -0.002    |
|                      | NF\(_3\) | 2.849      | 0         |
| O                    | NO   | 2.769      | -0.028    |
|                      | NO\(_2\) | 2.806      | 0.005     |
|                      | N\(_2\)O | 3.021      | -0.001    |
|                      | NF\(_3\) | 2.842      | -0.002    |
| OH                   | NO   | 1.809      | 0.08      |
|                      | NO\(_2\) | 1.666      | 0.073     |
|                      | N\(_2\)O | –         | –         |
|                      | NF\(_3\) | –         | –         |

\(^a\) The adsorption distance D refers to the shortest distance between the atom of gas and atom of substrate. \(^b\) The bond length change L, \( L = L_2 - L_1 \), \( L_1 \) and \( L_2 \) represents the chemical bond of gas before and after adsorption. A negative value indicates that the molecular bond length becomes shorter. \(^c\) The – symbol indicates that the chemical bond of the gas is broken and is not included in the measurement.
electron density after bonding and the atomic charge density at the corresponding point. By calculating and analyzing the deformation charge density, one can understand the bonding of the atoms in the system and the charge transfer during the bonding process. Figure 2 lists the deformation charge density diagrams for the NO, NO$_2$, N$_2$O, and NF$_3$ adsorption models (red represents electron gain, and blue represents electron loss). There is not much charge aggregation between the gas molecules and the atoms on the material surface, as shown in the four pictures below, indicating a weak bonding behavior between them. In addition, the charge transfer values in the adsorption structure are given in Table 2. NO, N$_2$O, and NF$_3$ lose 0.111 e, 0.008 e, and 0.014 e, respectively, while NO$_2$ gains 0.129 e from the surface of Ti$_3$C$_2$F$_2$, and NO and NO$_2$ have a large charge transfer in the process of adsorption.

Figure 1. The most stable adsorption structures of NO, NO$_2$, N$_2$O, and NF$_3$ on (a–h) Ti$_3$C$_2$F$_2$, (i–p) Ti$_3$C$_2$O$_2$, and (q–x) Ti$_3$C$_2$(OH)$_2$. (Light gray–Ti, dark grey–C, cyan–F, red–O, blue–N, white–H).
Table 2. Adsorption energy and charge transfer of gas molecules on Ti$_3$C$_2$Tx.

| Ti$_3$C$_2$Tx | Gas   | $E_{ads}$ (eV) | $Q_t$ $^a$ |
|--------------|-------|---------------|-----------|
| F            | NO    | −0.216        | 0.111     |
|              | NO$_2$ | −0.215        | −0.129    |
|              | N$_2$O | −0.273        | 0.008     |
|              | NF$_3$ | −0.323        | 0.014     |
| O            | NO    | −0.507        | 0.284     |
|              | NO$_2$ | −0.115        | 0.077     |
|              | N$_2$O | −0.240        | −0.008    |
|              | NF$_3$ | −0.386        | 0.036     |
| OH           | NO    | −1.709        | −0.607    |
|              | NO$_2$ | −3.806        | −0.753    |
|              | N$_2$O | −5.461        | −0.707    |
|              | NF$_3$ | −9.065        | −1.428    |

$^a$ A positive $Q_t$ means that the gas molecule loses electrons, and a negative $Q_t$ means that it gains electrons.

Electron density represents the probability of finding electrons at specific locations around atoms or molecules. The deformation charge density is the difference between the electron density after bonding and the atomic charge density at the corresponding point. By calculating and analyzing the deformation charge density, one can understand the bonding of the atoms in the system and the charge transfer during the bonding process. Figure 2 lists the deformation charge density diagrams for the NO, NO$_2$, N$_2$O, and NF$_3$ adsorption models (red represents electron gain, and blue represents electron loss). There is not much charge aggregation between the gas molecules and the atoms on the material surface, as shown in the four pictures below, indicating a weak bonding behavior between them. In addition, the charge transfer values in the adsorption structure are given in Table 2. NO, N$_2$O, and NF$_3$ lose 0.111 e, 0.008 e, and 0.014 e, respectively, while NO$_2$ gains 0.129 e from the surface of Ti$_3$C$_2$F$_2$, and NO and NO$_2$ have a large charge transfer in the process of adsorption.

![Deformation charge density diagrams](image)

**Figure 2.** Deformation charge density diagrams of (a) NO, (b) NO$_2$, (c) N$_2$O, (d) NF$_3$ on Ti$_3$C$_2$F$_2$ surface.

To further clarify the electronic structure characteristics of the adsorption systems, the total density of states (TDOS) and partial density of states (PDOS) of all adsorption systems are analyzed. The TDOS plots of Ti$_3$C$_2$F$_2$ after gas adsorption are shown in Figure 3. The
density of states of the whole system after the adsorption of NO and NO2 experiences a significant increase near the Fermi energy level, indicating that the adsorption of these two gases enhances the conductivity of the material. This phenomenon does not occur after the adsorption of N2O and NF3. As seen from the figure, the effects of N2O and NF3 on the whole adsorption system are below −3 eV, and the density of states of the whole system does not change greatly after adsorption. So, the adsorption of these two gases does not significantly enhance the conductivity of the material. These findings are consistent with the value of the charge transfer reflected in Table 2.

![Figure 3](image-url)  
**Figure 3.** Total electron density of states of Ti3C2F2 adsorbing NO, NO2, N2O, and NF3.

In the PDOS of Figure 4, only a small part of the orbital overlaps between the atoms of NO, NO2, and N2O and the atoms of the material surface, indicating that the interactions between the atoms are not strong. The F 2p orbital of NF3 has a partial overlap with the F 2p orbital of the surface around −7 eV, indicating that there are some interactions between them but not the formation of a strong chemical bond. Taking all the analyses together, the adsorption of the gases on the Ti3C2F2 surface is a physical adsorption, and there is no new chemical bond formed between the atoms composing the gas molecules and the atoms on the material surface.

![Figure 4](image-url)  
**Figure 4.** Partial electron density of states of Ti3C2F2 adsorbing (a) NO, (b) NO2, (c) N2O, (d) NF3.
3.2. Gas Adsorption on Ti$_3$C$_2$O$_2$

Figure 1i–p are top and side views of the four gas molecules after adsorption on the Ti$_3$C$_2$O$_2$ surface. The pictures show that there is no significant structural change in the gas and the substrate material after adsorption occurs, and the bond length changes of the gas molecules are measured, as shown in Table 1, which further confirms that there is only a slight change in the molecular structure after adsorption. Table 1 also shows that the gas adsorption distances are all within the range of 2.7 Å–3.1 Å. From the slight structural changes and large adsorption distances, it can be assumed that the adsorption of gases on Ti$_3$C$_2$O$_2$ is a physical adsorption. The adsorption energies of the four gases on the Ti$_3$C$_2$O$_2$ surface are given in Table 2 (−0.507 eV, −0.115 eV, −0.240 eV, and −0.386 eV for NO, NO$_2$, N$_2$O, and NF$_3$, respectively). All have negative adsorption energies, as in the case of adsorption on the Ti$_3$C$_2$F$_2$ surface, indicating that the adsorption of the gases does not require energy from outside.

The deformation charge density plots of the four adsorption systems are shown in Figure 5, which shows that the aggregation of electrons between the atoms of the four gases and the material surface is difficult due to the long adsorption distance, indicating that they have difficulty in forming chemical bonds with strong interactions. The charge transfer given in Table 2 shows that 0.284e is transferred from NO to Ti$_3$C$_2$O$_2$ surface, 0.077 e from NO$_2$ to Ti$_3$C$_2$O$_2$ surface, 0.008 e from Ti$_3$C$_2$O$_2$ surface to N$_2$O, and 0.036 e from NF$_3$ to Ti$_3$C$_2$O$_2$ surface. Compared with adsorption on Ti$_3$C$_2$F$_2$ surface, the changes of NO and NO$_2$ charge transfer are more obvious, with enhanced adsorption of NO and more charge transfer, and weakened adsorption of NO$_2$ and less charge transfer.

![Figure 5](image_url)

**Figure 5.** Deformation charge density diagram of (a) NO, (b) NO$_2$, (c) N$_2$O, (d) NF$_3$ on Ti$_3$C$_2$O$_2$ surface.

Figure 6 shows the TDOS of the whole adsorption system of Ti$_3$C$_2$O$_2$ after gas adsorption. Similar to Ti$_3$C$_2$F$_2$, after the adsorption of NO and NO$_2$, the density of states of the system experiences a significant increase near the Fermi energy level, which indicates that the adsorption of these two gases enhances the electrical conductivity of the material. Meanwhile, the adsorption of N$_2$O and NF$_3$ only makes the density of electronic states at some lower energy levels increase a little, and the effect on the density of states of the system is not great, which also reflects that NO and NO$_2$ have a larger charge transfer, and N$_2$O and NF$_3$ have a lower charge transfer. In the PDOS of Figure 7, only a small part of the orbital overlap between the atoms of NO, NO$_2$, and N$_2$O and the atoms of the material surface occurs at some energy levels, indicating a weak interaction between the atoms,
while the F 2p orbital of NF₃ has a partial overlap with the O 2p orbital of the surface at around −4.5 eV, indicating some interaction between them. In general, the adsorption of all the four gases on the Ti₃C₂O₂ surface is a physical adsorption.

![Figure 6. Total density of states of Ti₃C₂O₂ adsorbing NO, NO₂, N₂O, and NF₃.](image)

![Figure 7. Partial density of states of Ti₃C₂O₂ adsorbing (a) NO, (b) NO₂, (c) N₂O, (d) NF₃.](image)

### 3.3. Gas Adsorption on Ti₃C₂(OH)₂

The top and side views of the gases after adsorption on the best adsorption site on Ti₃C₂(OH)₂ are shown in Figure 1q–x. Unlike the adsorption on Ti₃C₂F₂ and Ti₃C₂O₂, it can be seen that after the adsorption of NO and NO₂, some H atoms around the gas molecules significantly deflect due to the attraction of the gas molecules. Other H atoms of the surface do not have different degrees of movement. The N atom of NO is attracted to the H on the surface in Figure 1r, and the O of NO₂ is attracted to the H on the surface in Figure 1t, and the bond angle has an obvious change. So, the adsorption distances of these two gases with the Ti₃C₂(OH)₂ surface shown in Table 1 are significantly smaller than those of Ti₃C₂F₂ and Ti₃C₂O₂. In addition, the bond length changes of the gases in Table 1 are...
also greater due to the stronger interactions between the gas and the surface. This strong adsorption is even more significant after the adsorption of N$_2$O and NF$_3$. Figure 1u,w show that the H atoms on the Ti$_3$C$_2$(OH)$_2$ surface are stripped from the surface and form new chemical bonds with the atoms of gases. The N$_2$O reacts with the H atoms of the surface to form H$_2$O and N$_2$. After NF$_3$ adsorbs on the surface, two HF molecules form. All these figures indicate a stronger chemisorption occurring among them. The adsorption energies in Table 2 also reflect the phenomena above. It shows NF$_3$ having the strongest interaction with the surface, with an adsorption energy of $-9.065$ eV, followed by N$_2$O with an adsorption energy of $-5.461$ eV, and finally NO$_2$ and NO with adsorption energies of $-3.806$ eV and $-1.709$ eV, respectively. Compared to the previous two materials with different terminal groups, the adsorption between four gases and Ti$_3$C$_2$(OH)$_2$ is enhanced in different degrees.

The interaction of the gas molecules with the Ti$_3$C$_2$(OH)$_2$ surface is further analyzed by deformation charge density, and the deformation charge density diagram of the adsorption system is shown in Figure 8. The N atom of NO in Figure 8a is closer to the H atom on the surface, and the red charge aggregation shown between them indicates a stronger interaction. Combined with Table 2, 0.607 e is transferred from the Ti$_3$C$_2$(OH)$_2$ surface to NO. There is also more charge aggregation between the O atom of NO$_2$ and the H atom on the surface in Figure 8b, with 0.753 e transferred from the Ti$_3$C$_2$(OH)$_2$ surface to NO$_2$. In Figure 8c,d, it can be seen that a large amount of charge aggregates between the H atoms, which are removed from the surface, and the atoms of the gas, further demonstrating the formation of chemical bonds between them, accompanied by 0.707 e and 1.428 e transferring from Ti$_3$C$_2$(OH)$_2$ to N$_2$O and NF$_3$.

![Deformation charge density diagram of (a) NO, (b) NO$_2$, (c) N$_2$O, (d) NF$_3$ on Ti$_3$C$_2$(OH)$_2$ surface.](image)

The TDOS of Ti$_3$C$_2$(OH)$_2$ after gas adsorption is shown in Figure 9. Apparently, the density of states of the whole system before and after the adsorption of NO, NO$_2$, N$_2$O, and NF$_3$ experiences a great change. It can be clearly seen that all the TDOS show a right shift, and the electronic states of the system move to higher energy levels after the adsorption of these gases, indicating that the adsorption of the gases has a relatively large effect on the adsorption system, and the densities of states all increase around the Fermi energy level, meaning that the conductivity of the material is enhanced. All these changes are consistent with the large charge transfer between the gases and Ti$_3$C$_2$(OH)$_2$. In addition, after the
adsorption of NF$_3$, a new peak at $-4.5$ eV clearly appears, which changes the whole system the most, which also reflects the strongest interaction of NF$_3$ with Ti$_3$C$_2$(OH)$_2$.

Figure 10 shows the PDOS for some gas atoms and surface atoms. The N 2p orbital of NO and the H 1s orbital from the surface have the same density of state peaks at 0 eV, $-9$ eV in Figure 10a, which indicates a resonance of the electrons in the orbital, a manifestation of a stronger interaction. The O 2p orbital of NO$_2$ and the H 1s orbital at 0 eV, $-8$ eV, $-9$ eV have an overlap in Figure 10b, which likewise indicates a stronger interaction between them, and the O 2p orbital of N$_2$O and the H 1s orbital of the surface have the same density of state peaks at $-6.5$ eV, $-9$ eV in Figure 10c, demonstrating that O–H bonds are indeed formed between O and H. The N 2p and F 2p orbitals of NF$_3$ and the H1 1s and H2 1s of the surface likewise show multiple overlaps in Figure 10d, representing the formation of N–H bonds and F–H bonds.

Figure 10. Partial electron density of states of Ti$_3$C$_2$(OH)$_2$ adsorbing (a) NO, (b) NO$_2$, (c) N$_2$O, (d) NF$_3$.
In summary, the adsorption that occurs on the Ti$_3$C$_2$(OH)$_2$ surface is significantly different from that of Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$O$_2$, which has greater adsorption energy, more charge transfer, and stronger interactions. The reason is that the hydroxyl groups on the surface are more chemically active than oxygen and fluorine atoms, and the gas molecules interact more strongly with the OH surface. When NO and NO$_2$ make contact with the Ti$_3$C$_2$(OH)$_2$ surface, N and O are attracted by OH and form O–H···N and O–H···O hydrogen bonds, respectively. When N$_2$O and NF$_3$ make contact with the Ti$_3$C$_2$(OH)$_2$ surface, O atoms, N atoms, and F atoms are attracted by OH, forming O–H···O, O–H···N, and O–H···F hydrogen bonds and approaching to the surface, which eventually leads to H atom stripping from surface and forming new chemical bonds.

3.4. Ti$_3$C$_2$Tx Gas Sensing Performance Evaluation

An important parameter reflecting the sensing performance is the recovery time $\tau$, which represents the time required to remove the adsorbed gas molecules from the material surface, defined as [30]

$$\tau = \frac{E_{ads}}{kT}$$

$v_0$ indicates the attempt frequency, assuming that all gases have the same order of magnitude as that of NO$_2$ ($1.0 \times 10^{12}$ s$^{-1}$) [31]; $E_{ads}$ is the energy barrier for desorption, which is set equal to the adsorption energy; $k$ is the Boltzmann constant (8.62 × 10$^{-5}$ eV·K$^{-1}$); and $T$ is the Kelvin temperature. It can be seen from the equation that the larger the adsorption energy is for a gas molecule, the more difficult its desorption will become accordingly. The recovery time of each gas on Ti$_3$C$_2$Tx at room temperature is given in Table 3. The adsorption energies on Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$O$_2$ are generally small, so they reflect a fast recovery time, and the slowest is 0.37 ms for NO adsorption on Ti$_3$C$_2$O$_2$, and the very short recovery time may not achieve effective detection in the actual sensing detection. In contrast, the adsorptions of four gases on Ti$_3$C$_2$(OH)$_2$ have a large adsorption energy and exhibit a long recovery time. It is difficult for gas molecules to desorb from the material surface at room temperature, which is not conducive to the reuse of the sensor but has potential value as a gas adsorbent. The desired sensor performance can be achieved by surface modification. There are many ways of surface modification, such as controlling the ratio of surface F, O and OH groups, doping with other metals and their compounds, adding atomic vacancies, adding other terminal groups, etc. [32–36].

### Table 3. Recovery time at room temperature (25 °C).

| Ti$_3$C$_2$Tx | $\tau$(NO)/s | $\tau$(NO$_2$)/s | $\tau$(N$_2$O)/s | $\tau$(NF$_3$)/s |
|--------------|--------------|-----------------|-----------------|-----------------|
| F            | $4.4 \times 10^{-9}$ | $3.9 \times 10^{-9}$ | $4.1 \times 10^{-8}$ | $2.8 \times 10^{-7}$ |
| O            | $3.7 \times 10^{-4}$ | $8.8 \times 10^{-11}$ | $1.1 \times 10^{-8}$ | $3.3 \times 10^{-6}$ |
| OH           | $7.8 \times 10^{16}$ | $2.2 \times 10^{52}$ | $2.1 \times 10^{80}$ | $1.8 \times 10^{141}$ |

4. Conclusions

In this paper, the adsorption process of gases on the surface of these materials was studied by constructing the adsorption models of NO, NO$_2$, N$_2$O, and NF$_3$ on Ti$_3$C$_2$Tx with three terminal groups of F, O, and OH, and the adsorption behavior of gases was analyzed according to adsorption energy, charge density, and density of states through DFT calculations:

1. The adsorption energies of NO on Ti$_3$C$_2$F$_2$, Ti$_3$C$_2$O$_2$, and Ti$_3$C$_2$(OH)$_2$ are $-0.216$ eV, $-0.507$ eV, and $-1.709$ eV, respectively, and the charge transfers are $0.111$ e, $0.284$ e, and $-0.607$ e, respectively. After NO adsorption, the density of states of the adsorbed systems all increase near the Fermi energy level, and conductivity is enhanced.

2. The adsorption energies of NO$_2$ on Ti$_3$C$_2$F$_2$, Ti$_3$C$_2$O$_2$, and Ti$_3$C$_2$(OH)$_2$ are $-0.213$ eV, $-0.115$ eV, and $-3.806$ eV, respectively, and the charge transfer is $-0.129$ e, $0.077$ e,
and $-0.753$ e, respectively, and the adsorption of NO$_2$ leads to the enhancement of electrical conductivity of the materials.

(3) The adsorption energies of N$_2$O on Ti$_3$C$_2$F$_2$, Ti$_3$C$_2$O$_2$, and Ti$_3$C$_2$(OH)$_2$ are $-0.273$ eV, $-0.240$ eV, and $-5.461$ eV, respectively, with charge transfer of $0.008$ e, $-0.008$ e, and $-0.7007 e$. After the adsorption of N$_2$O, only Ti$_3$C$_2$(OH)$_2$ exhibits an increase in electrical conductivity, and it is the chemisorption that occurs with strong interactions.

(4) The adsorption energies of NF$_3$ on Ti$_3$C$_2$F$_2$, Ti$_3$C$_2$O$_2$, and Ti$_3$C$_2$(OH)$_2$ are $-0.323$ eV, $-0.386$ eV, and $-9.065$ eV, respectively, and the charge transfers are $0.014$ e, $0.036$ e, and $-1.428$ e, respectively. NF$_3$ exhibits strong chemisorption only on Ti$_3$C$_2$Ts terminated with -OH, accompanied by a large amount of charge transfer.

(5) The adsorption of all four gases on the surface of Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$O$_2$ exhibits short recovery times, while the adsorption on the surface of Ti$_3$C$_2$(OH)$_2$ makes it difficult to achieve desorption at room temperature due to the stronger adsorption effect.

Combining all the analyses, Ti$_3$C$_2$Ts with three terminal groups has good sensing ability for NO and NO$_2$, while Ti$_3$C$_2$Ts with -OH surface has great adsorption energy and significant charge transfer for NO, NO$_2$, N$_2$O, NF$_3$, which makes it easy to achieve gas detection, but it is also found to have the disadvantage of long recovery time, so the performance of the material needs to be improved by further methods.

Supplementary Materials: The following are available online at https://www.mdpi.com/1033-124X/12/12/2311/s1. Figure S1. Molecule structures of NO, NO$_2$ and NF$_3$.

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