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# Simultaneous adsorption of SO<sub>2</sub> and CO<sub>2</sub> in an Ni(bdc)(ted)<sub>0.5</sub> metal–organic framework†

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The metal–organic framework Ni(bdc)(ted)<sub>0.5</sub> is a promising material for simultaneous capture of harmful gases such as SO<sub>2</sub> and CO<sub>2</sub>. We found that SO<sub>2</sub> performs much better than CO<sub>2</sub> during adsorption, and the lack of physical insight was clarified through detailed analyses of the electronic structures obtained from density functional theory calculations. Our results showed that strong interactions of the d band of Ni atoms with the valence states (2n, 3n, and 4n) of SO<sub>2</sub> but almost not with those of CO<sub>2</sub> are the main reasons. Our finding is useful for the rational design of new metal–organic frameworks with suitable interactions for the simultaneous capture of not only SO<sub>2</sub> and CO<sub>2</sub> but also other gases.

## I. Introduction

CO<sub>2</sub> is a greenhouse gas leading to global warming, and SO<sub>2</sub> is the primary source of acid rain.<sup>1,2</sup> With increasing consumption of fossil fuel energies, emissions of SO<sub>2</sub> and CO<sub>2</sub> are becoming more serious. The removal of these gases is, therefore, an active research area attracting much attention from scientists. Among the proposed materials and techniques,<sup>3–6</sup> metal–organic frameworks (MOFs) are the most promising candidates that satisfy the practical requirements of high stability, high gas uptake capacity, low energy of gas desorption, and low cost.

Due to exceptionally high surface area, tunable porous crystals, and structural versatility, MOFs exhibit excellent ability for the capture and selective separation of a wide range of gases based on adsorption.<sup>7</sup> Particularly, MOF-200 and MOF-210 have shown the highest CO<sub>2</sub> uptake so far up to more than 70 wt%.<sup>8</sup> Several studies have also been devoted to the study of SO<sub>2</sub> capture using MOFs.<sup>9–14</sup> Because of the co-existence of SO<sub>2</sub> and CO<sub>2</sub> in the same practical environment and the need for the removal of these gases to mitigate their influences on the climate, the simultaneous capture of the gases within the same MOF is particularly important.<sup>6,15–18</sup> Recently, Tan and coworkers found that Ni(bdc)(ted)<sub>0.5</sub> (bdc = benzenedicarboxylate, ted = triethylenediamine) can adsorb a significant amount of SO<sub>2</sub> (9.97 mmol g<sup>−1</sup>) and simultaneously exhibit remarkable uptake of CO<sub>2</sub> at low pressure and ambient temperature.<sup>13,19,20</sup> Remarkably, SO<sub>2</sub> performs much better than CO<sub>2</sub> during co-adsorption by Ni(bdc)(ted)<sub>0.5</sub> as SO<sub>2</sub> can replace

pre-adsorbed CO<sub>2</sub>,<sup>13</sup> however, the physical insights into this phenomenon remain unexplained.

Here, we used van der Waals-corrected density functional theory,<sup>21–24</sup> which has been successfully applied in previous studies,<sup>25–27</sup> to reveal the electronic nature of MOF-gas interactions. Thus, our study is necessary, and the current findings are useful for the design of new MOFs for simultaneous adsorption of other gases.

## II. Computational details

Density functional theory calculations were performed using the Vienna Ab Initio Simulation Package. The exchange and correlation functionals<sup>21,28</sup> including the van der Waals dispersion corrections, vdW-DF,<sup>22,29</sup> were used in this study. The electron-ion interactions were described by the projector augmented-wave method<sup>23,24</sup> with a plane wave cut-off of 700 eV. The integration over the Brillouin zone was calculated using the Monkhorst–Pack scheme<sup>30</sup> with *k*-point sampling of 5 × 5 × 5 for geometry optimization and electronic structure calculations. The size and shape of the unit cell of Ni(bdc)(ted)<sub>0.5</sub> were fully optimized; it exhibited a tetragonal structure with cell parameters of *a* = *b* = 11.15 Å and *c* = 9.53 Å (Fig. 1).<sup>13</sup> Spin polarization was performed for geometry optimization and total energy calculation.

The adsorption energy *E*<sub>ad</sub> is defined as follows:

$$E_{\text{ad}} = E_{\text{MOF+SO}_2/\text{CO}_2} - E_{\text{MOF}} - E_{\text{SO}_2/\text{CO}_2}. \quad (1)$$

Here, *E*<sub>MOF+SO<sub>2</sub>/CO<sub>2</sub></sub>, *E*<sub>MOF</sub>, *E*<sub>SO<sub>2</sub></sub>, and *E*<sub>CO<sub>2</sub></sub> are the total energies of the MOF + gas system, MOF Ni(bdc)(ted)<sub>0.5</sub>, isolated SO<sub>2</sub>, and isolated CO<sub>2</sub>, respectively.

The charge density difference<sup>31–33</sup> was calculated for the most stable configurations of the adsorbed SO<sub>2</sub> and CO<sub>2</sub> using the following formula:

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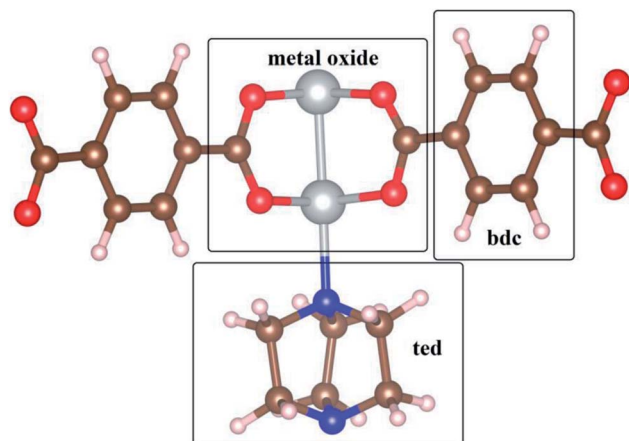


Fig. 1 The unit cell of Ni(bdc)(ted)<sub>0.5</sub>; C (brown), O (red), H (white), N (blue), and Ni (silver).

$$\Delta\rho = \rho_{\text{MOF}+\text{SO}_2/\text{CO}_2} - \rho_{\text{MOF}} - \rho_{\text{SO}_2/\text{CO}_2} \quad (2)$$

Here,  $\rho_{\text{MOF}+\text{SO}_2/\text{CO}_2}$  and  $\rho_{\text{MOF}}$  are the charge densities of the MOF + gas system and MOF Ni(bdc)(ted)<sub>0.5</sub>, respectively;  $\rho_{\text{SO}_2}$  and  $\rho_{\text{CO}_2}$  are the charge densities of the single molecule SO<sub>2</sub> and CO<sub>2</sub>, respectively. Here, the charge density of the MOF and the gas was calculated from the corresponding structures obtained from the MOF + gas system by removing either the gas or the MOF, respectively.

The partial point charges for each atom of SO<sub>2</sub> and CO<sub>2</sub> and MOF were estimated using the Bader charge partition method.<sup>34,35</sup>

### III. Results and discussion

We label the unit cell surface of Ni(bdc)(ted)<sub>0.5</sub> by three main regions: bdc, ted, and metal oxide (Fig. 1). For single gas adsorption, we load each molecule of SO<sub>2</sub> and CO<sub>2</sub> to various positions on the surface of Ni(bdc)(ted)<sub>0.5</sub>. We then optimize the geometry and calculate the adsorption energy of SO<sub>2</sub> and CO<sub>2</sub>. We select the most stable configuration of SO<sub>2</sub> and CO<sub>2</sub> in each surface region based on the obtained adsorption energy, as presented in Fig. 2, for further analyses. This figure also exhibits the bond distances between SO<sub>2</sub> and CO<sub>2</sub> with the nearest atoms of Ni(bdc)(ted)<sub>0.5</sub>. To roughly understand the nature of MOF-gas interaction, we analyze the bond distance between the gas and the MOF. In this study, the atomic radii are defined through the Wigner-Seitz radius, which are 0.37, 0.741, 0.783, 0.863, 0.953, and 1.286 Å for H, O, N, C, S, and Ni, respectively. Generally, the length of a covalent bond between two atoms equals the sum of the radii of the two atoms. If there are covalent bonds, the standard bond lengths of C-S, O-H, S-O, C-C, and C-O between the gas and MOF, as shown in Fig. 2, are expected to be 1.816, 1.111, 1.694, 1.726, and 1.602 Å, respectively. However, the nearest bond distances (Fig. 2) are much longer than these standard covalent bond lengths. Therefore, there is physical interaction rather than a covalent bond between the gases and MOF.

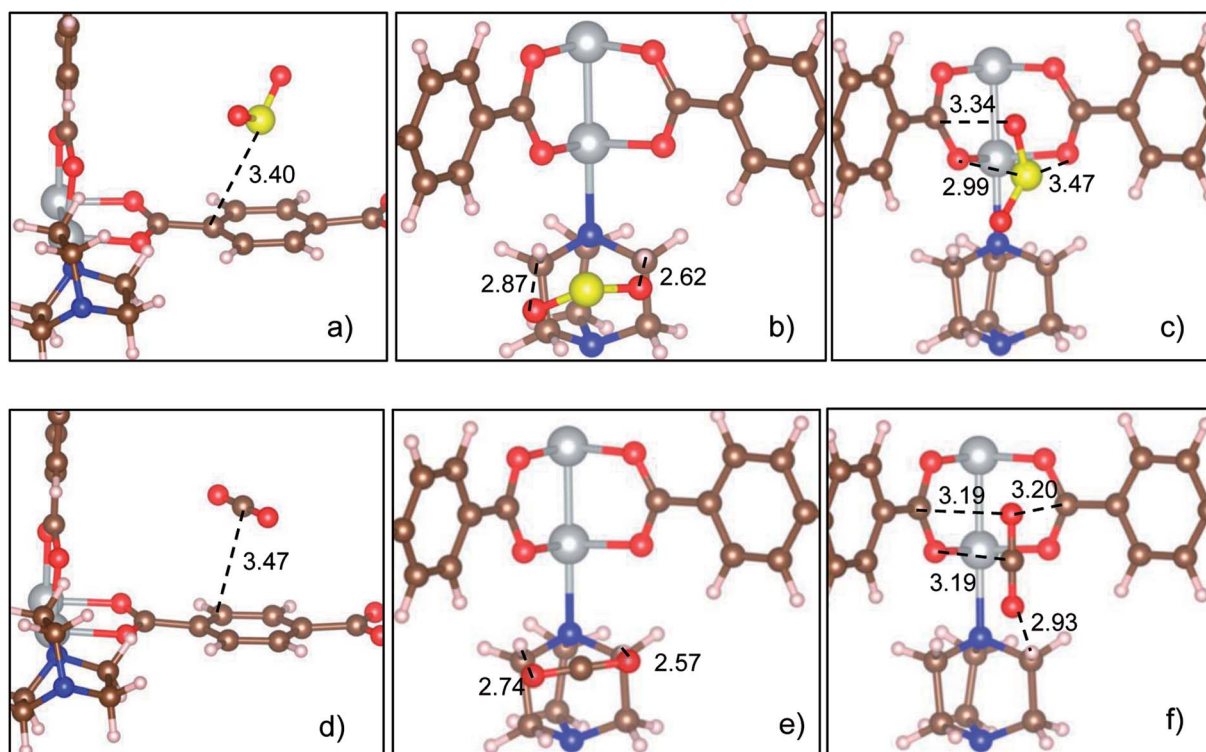
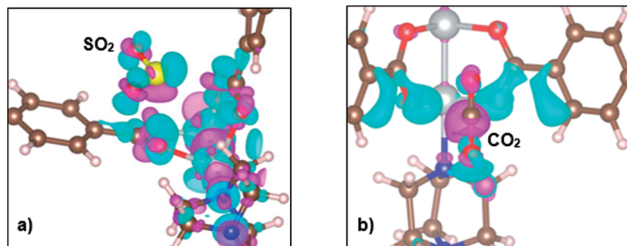


Fig. 2 Stable adsorption configurations of SO<sub>2</sub> (upper panel) and CO<sub>2</sub> (lower panel) on bdc (a and d), ted (b and e), and metal oxide (c and f) of Ni(bdc)(ted)<sub>0.5</sub>; C (brown), O (red), H (white), S (yellow), N (blue), and Ni (silver). The bond distance is in angstroms.



**Table 1** Adsorption Energy (eV) of SO<sub>2</sub> and CO<sub>2</sub> in Ni(bdc)(ted)<sub>0.5</sub>

Adsorption site	bdc	ted	Metal oxide
SO <sub>2</sub>	−0.351	−0.469	−1.010
CO <sub>2</sub>	−0.213	−0.307	−0.380

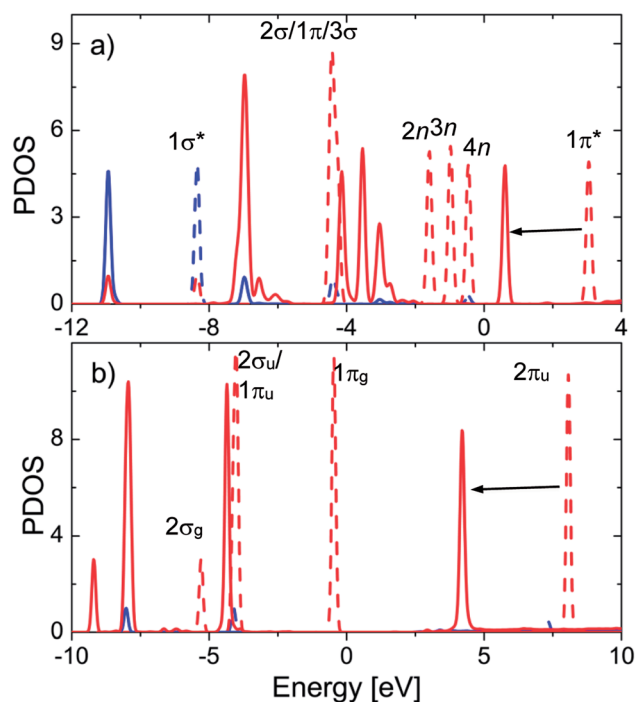
**Fig. 3** The charge density difference of the most stable configuration of SO<sub>2</sub> (a) and CO<sub>2</sub> (b) found on the metal oxide. Pink and cyan clouds denote the charge loss and gain, respectively.**Table 2** Bader charges (e<sup>−</sup>) of the adsorbed SO<sub>2</sub> and CO<sub>2</sub> and the MOF compared to those of the isolated ones, where (−) represents the charge loss and (+) represents the charge gain

Adsorption site	bdc	ted	Metal oxide
S	−0.013	+0.002	−0.032
2O	+0.055	+0.108	+0.102
<b>SO<sub>2</sub></b>	<b>+0.042</b>	<b>+0.110</b>	<b>+0.070</b>
20H	−0.032	−0.094	−0.005
22C	−0.005	+0.011	−0.064
2N	0.000	+0.010	−0.010
8O	−0.005	−0.032	+0.068
2Ni	0.000	−0.005	−0.058
<b>MOF</b>	<b>−0.042</b>	<b>−0.110</b>	<b>−0.070</b>
C	−0.019	−0.048	−0.066
2O	+0.036	+0.055	+0.087
<b>CO<sub>2</sub></b>	<b>+0.017</b>	<b>+0.008</b>	<b>+0.021</b>
20H	−0.019	−0.022	−0.030
22C	+0.008	+0.009	+0.005
2N	−0.002	0.000	0.000
8O	−0.003	+0.004	+0.001
2Ni	0.000	0.000	+0.003
<b>MOF</b>	<b>−0.017</b>	<b>−0.008</b>	<b>−0.021</b>

Table 1 shows that the adsorption strengths of both gases follow the order bdc < ted < metal oxide, which agrees with the results for SO<sub>2</sub> in a previous study.<sup>13</sup> The adsorption energy of SO<sub>2</sub> is significantly lower than that of CO<sub>2</sub> for each adsorption site, indicating that SO<sub>2</sub> adsorbs more strongly than CO<sub>2</sub>. Furthermore, while the adsorption energies of CO<sub>2</sub> on the sites are not much different, those of SO<sub>2</sub> vary largely, especially on metal oxide, which implies that the metal center of Ni(bdc)(ted)<sub>0.5</sub> has a more significant influence on SO<sub>2</sub> than on CO<sub>2</sub>.<sup>13</sup> A stronger binding energy of SO<sub>2</sub> compared with that of CO<sub>2</sub> at the metal site is also observed for other MOFs;<sup>20,36,37</sup> the binding energy of SO<sub>2</sub> and CO<sub>2</sub> at the metal oxide of

Ni(bdc)(ted)<sub>0.5</sub> is found to be in the same order with that of Mg, Ni, and Co-MOF-74.<sup>20</sup> However, no comprehensive explanations based on the analysis of electronic structures have been provided for the current MOF system. Besides, vibrational energy also influences the stability of the adsorbed gases. Therefore, we calculate the vibrational frequency ( $\omega$ ) and the vibrational energy ( $1/2 h\omega$ ) for the adsorbed SO<sub>2</sub> and CO<sub>2</sub>. The frequencies of the three strongest vibrational modes on the metal oxide are found to be 1240, 1071, and 505 cm<sup>−1</sup> for SO<sub>2</sub> and 2432, 1366, and 610 cm<sup>−1</sup> for CO<sub>2</sub>. For the other adsorption sites, the frequencies fluctuate around these values by less than 50 cm<sup>−1</sup>. The obtained frequencies agree well with the experimental data.<sup>13,20,38</sup> Sequentially, the calculated vibrational energies are 0.154, 0.133, and 0.063 eV for SO<sub>2</sub> and 0.301, 0.169, and 0.076 eV for CO<sub>2</sub>. The vibrational energy of the strongest SO<sub>2</sub> mode (0.154 eV) is significantly smaller than the adsorption energy difference (0.541 eV) between SO<sub>2</sub> on metal oxide and ted, whereas that of CO<sub>2</sub> (0.301 eV) is much higher than its adsorption energy difference (0.073 eV) between these sites. Therefore, fluctuation cannot cause transition between the most favorable adsorption sites of SO<sub>2</sub>, but it exhibits effects on CO<sub>2</sub>. This result implies that SO<sub>2</sub> is much more stable compared to CO<sub>2</sub> toward fluctuation.

Next, we systematically clarify the electronic structure of MOF – gas interaction. The charge density difference between SO<sub>2</sub> and CO<sub>2</sub> on the metal oxide is presented in Fig. 3a and b, respectively. The charge density difference is calculated by using eqn (2). The charge donation from SO<sub>2</sub> and CO<sub>2</sub> to MOF is depicted by the charge depletion cloud, whereas the back-donation from MOF to SO<sub>2</sub> and CO<sub>2</sub> is indicated by the

**Fig. 4** The partial DOS of the isolated (dashed line) and adsorbed (solid line) gases SO<sub>2</sub> (a) and CO<sub>2</sub> (b) on the metal oxide. The s and p orbitals are presented in blue and red, respectively.

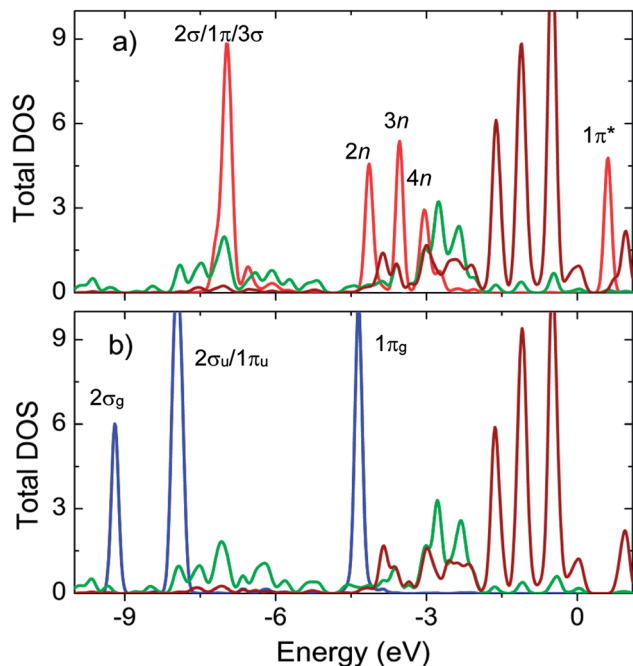


Fig. 5 The total DOS of the adsorbed  $\text{SO}_2$  (red) and the adsorbed  $\text{CO}_2$  (blue) on the metal oxide. The total DOS of the MOF's oxygen atoms and the d band of the Ni atoms are presented in green and brown, respectively.

charge accumulation on  $\text{SO}_2$  and  $\text{CO}_2$ . A large extent of charge redistribution is found on Ni atoms in the case of  $\text{SO}_2$  but not for  $\text{CO}_2$ , which is consistent with the observations from adsorption energy. The positive sign of the total point charge for

the adsorbed  $\text{SO}_2$  and  $\text{CO}_2$  (Table 2) implies that back-donation is stronger than donation. The charge gains of the gases are mainly distributed on the oxygen atoms, and the charge gain of  $\text{SO}_2$  is greater than that of  $\text{CO}_2$  for all adsorption sites.

The donation of charge occurs at MOF hydrogen atoms for both  $\text{SO}_2$  and  $\text{CO}_2$  adsorptions and also at MOF C atoms for  $\text{CO}_2$  adsorption for all the adsorption sites. The other MOF atoms gain or donate charge or remain neutral depending on the local sites.

Fig. 4a shows substantial expansion in the width and significant variation in the peak height of all the valence states ( $2\sigma/1\pi/3\sigma$ ,  $2n$ ,  $3n$ , and  $4n$ ) of  $\text{SO}_2$ . Scheme S1 and S2 in the ESI† depict the molecular orbital diagrams of  $\text{SO}_2$  and  $\text{CO}_2$ . On the basis of these schemes, we located the peaks of electronic density of the states of  $\text{SO}_2$  and  $\text{CO}_2$ . The modification of  $2\sigma/1\pi/3\sigma$  states is mainly ascribed to (Fig. 5a) the overlap between DOS of  $\text{SO}_2$  and that of MOF oxygen atoms, whereas the change in the  $2n/3n/4n$  states is ascribed to the interaction of DOS of  $\text{SO}_2$  with that of MOF oxygen atoms and the d band of Ni atoms.

Fig. 4b shows that the DOS peaks of  $\text{CO}_2$  shifted to a lower energy level and the intensity of  $2\sigma_u/1\pi_u/1\pi_g/2\pi_u$  states decreased upon adsorption, which was closely correlated to the overlap of these orbitals with those of the MOF oxygen atoms (Fig. 5b). The shift in the value of the energy level is about 2.5 eV for  $\text{SO}_2$  and 4.0 eV for  $\text{CO}_2$ . Noticeably, there is no significant interaction between the states of  $\text{CO}_2$  and the d band of the Ni atoms, which is entirely different from the case of  $\text{SO}_2$ . We also provide a detailed analysis of the interaction between  $\text{SO}_2$  and  $\text{CO}_2$  with bdc and ted in the following section.

For  $\text{SO}_2$  on bdc, Fig. 6a shows that the peaks of DOS of  $\text{SO}_2$  exhibit the same shape as that of isolated  $\text{SO}_2$  with weaker

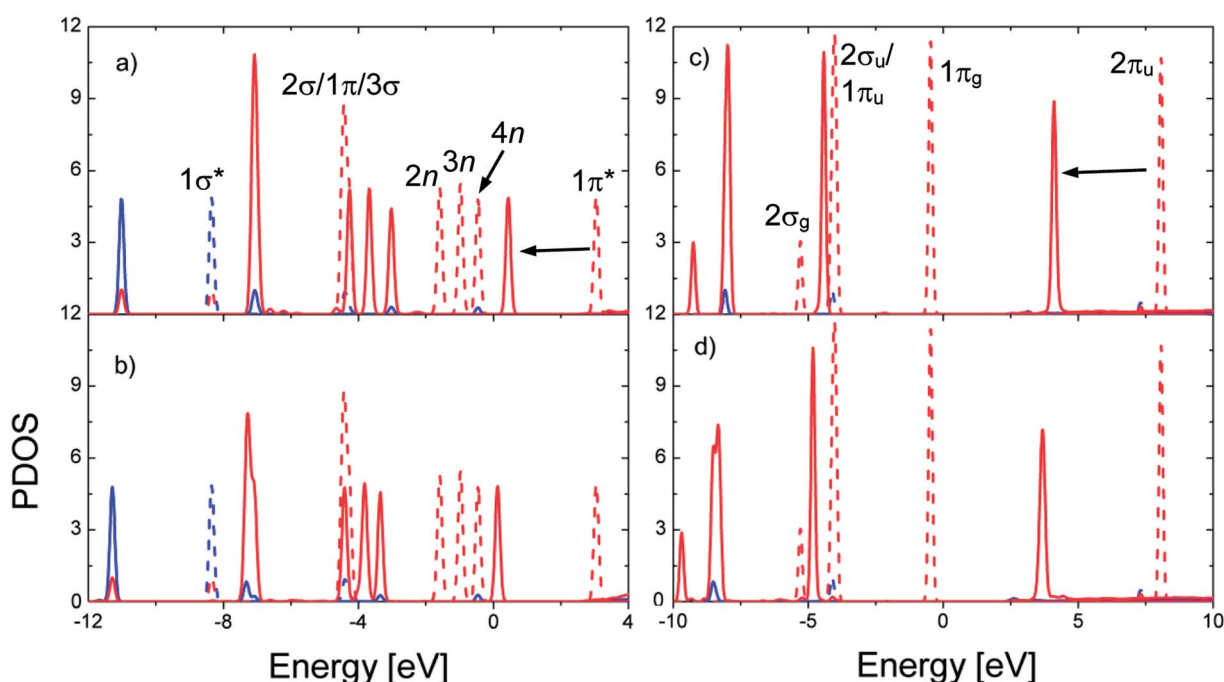


Fig. 6 The partial DOS of the adsorbed gases (solid line) and the isolated gases (dotted line) for  $\text{SO}_2$  (left side) and  $\text{CO}_2$  (right side): on bdc (a and c), on ted (b and d). The s and p states are presented in blue and red, respectively.





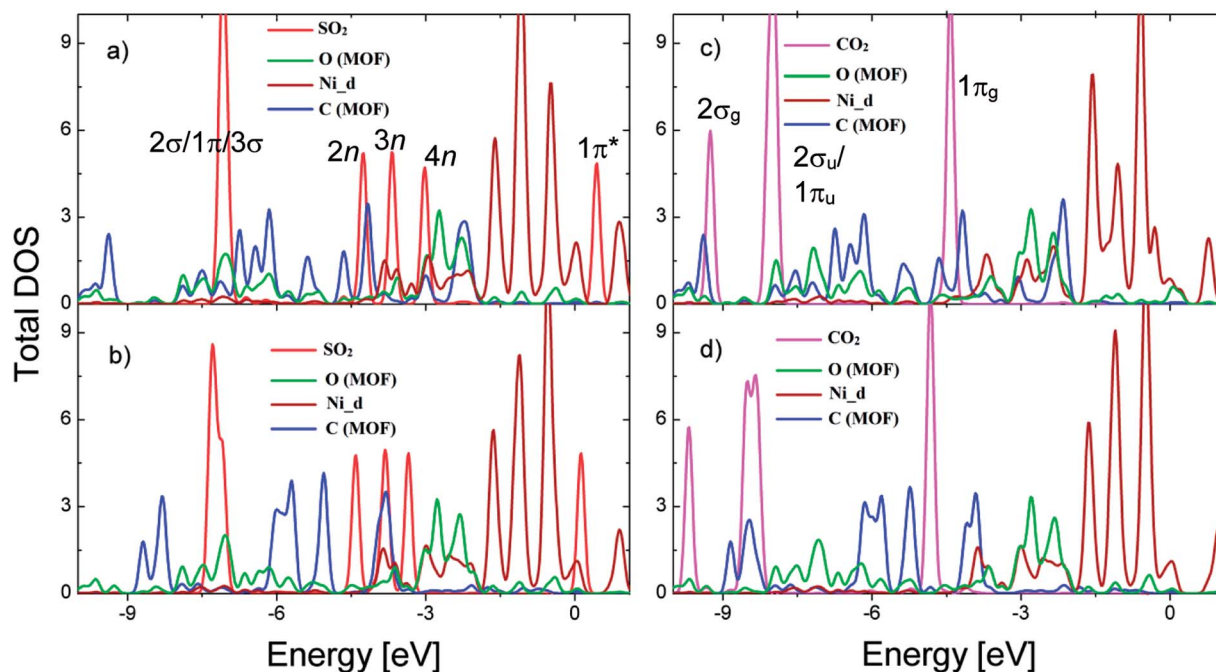


Fig. 7 The total DOS of adsorbed  $\text{SO}_2$  (left side), adsorbed  $\text{CO}_2$  (right side), and atoms of  $\text{Ni}(\text{bdc})(\text{ted})_{0.5}$  on bdc (a and c), ted (b and d). The d band of the Ni atoms strongly interacts with the valence states of  $\text{SO}_2$  but almost does not interact with the valence states of  $\text{CO}_2$  for all the adsorption sites.

interactions between  $\text{SO}_2$  and bdc compared with those observed on other adsorption sites. The height of the peak of  $2\sigma/1\pi/3\sigma$  states is enhanced, whereas that of the  $4n$  state is slightly reduced because of the overlap of these states with DOS of the MOF atoms (Fig. 7a). For  $\text{SO}_2$  on ted, as presented in Fig. 6b, the width and height of  $2\sigma/1\pi/3\sigma$  and  $2n/3n$  states are modified owing to the interactions with the hydrogen and carbon atoms of ted (Fig. 7b). In particular, overlaps occur between the  $2\sigma/1\pi/3\sigma/2n$  states and the states of the oxygen atoms and between the  $3n$  state and the states of the MOF carbon atoms and the d band of Ni atoms. Moreover, the  $1\pi^*$  peak shifts to the Fermi level due to the overlap with the d band of Ni atoms; therefore,  $\text{SO}_2$  gains a significantly greater charge on ted than on bdc and metal oxide (Table 2).

For  $\text{CO}_2$ , the position of the peaks shifts to a lower energy, and the height of the peaks is reduced upon adsorption (Fig. 6c

and d). However, the shape of the peaks is almost unchanged except for the modification at the  $2\sigma_u/1\pi_u$  states for the adsorption on ted (Fig. 6d) due to the overlap of these states with the states of ted's carbon atoms (Fig. 7d). For  $\text{CO}_2$  on all the adsorption sites, the interaction with MOF is accomplished through the overlaps of DOS of  $\text{CO}_2$  with DOS of the MOF C and O atoms. Noticeably, there is no significant interaction between  $\text{CO}_2$  and the Ni atoms for all the adsorption sites, which is different from that observed for  $\text{SO}_2$ .

For the simultaneous adsorption of  $\text{SO}_2$  and  $\text{CO}_2$  in  $\text{Ni}(\text{bdc})(\text{ted})_{0.5}$ , we found their most favorable adsorption configurations (Fig. 8). The adsorption energies are  $-0.33$ ,  $-0.65$ , and  $-0.41$  eV for configurations (a), (b), and (c), respectively. Therefore, the configuration (b) is the most favorable one. Fig. 9 shows that the DOS of  $\text{SO}_2$  and  $\text{CO}_2$  show similar characteristics to those of single gas adsorption. From the above

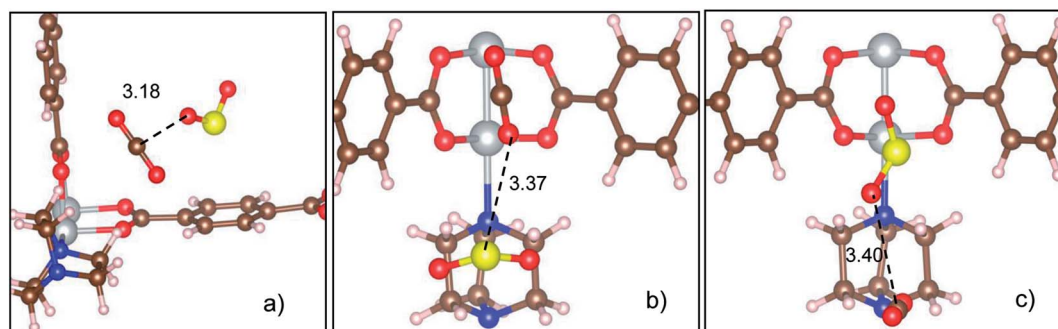


Fig. 8 The most stable configurations for co-adsorption of  $\text{SO}_2$  and  $\text{CO}_2$ . The co-adsorption energies are  $-0.33$ ,  $-0.65$ , and  $-0.41$  eV for (a), (b), and (c), respectively; C (brown), O (red), H (white), S (yellow), N (blue), and Ni (silver). The bond distance is in angstroms.



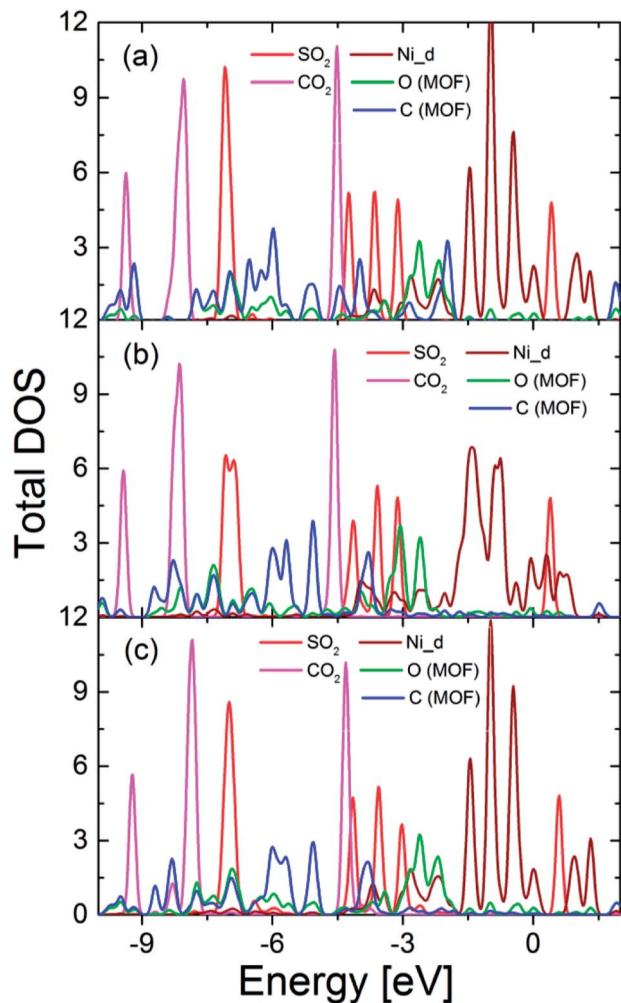


Fig. 9 The total DOS of adsorbed SO<sub>2</sub>, adsorbed CO<sub>2</sub>, and atoms of Ni(bdc)(ted)<sub>0.5</sub> for co-adsorption of SO<sub>2</sub> and CO<sub>2</sub>; (a), (b), and (c) correspond to the configurations presented in Fig. 8.

analyses, we can see that while both SO<sub>2</sub> and CO<sub>2</sub> interact with the MOF C and O atoms, only SO<sub>2</sub> significantly interacts with Ni atoms. Thus, we can state that the participation of the d band to different extents can be the reason for competition of SO<sub>2</sub> and CO<sub>2</sub> in Ni(bdc)(ted)<sub>0.5</sub>. Our findings support the previous experimental results about the crucial role of metal centers.<sup>13,25</sup> This manuscript is devoted to providing an explanation for the experimental observation regarding the co-adsorption of SO<sub>2</sub> and CO<sub>2</sub> in Ni(bdc)(ted)<sub>0.5</sub>. Therefore, the study with different organic linkers, metal centers, and gas mixtures is beyond the scope of the present research and will be addressed<sup>39–41</sup> in upcoming studies.

## IV. Conclusion

In conclusion, DOS of both gases homogeneously shift to lower energy levels upon adsorption. The deformations are more profound in the DOS of SO<sub>2</sub> than that of CO<sub>2</sub>, including the downshifting of the anti-bonding  $1\pi^*$  state of SO<sub>2</sub> to the Fermi level. The charge gain of SO<sub>2</sub> is higher than that of CO<sub>2</sub>, which is

consistent with the adsorption energy trend. Notably, the adsorption energy of SO<sub>2</sub> is significantly greater on metal oxide than on other adsorption sites, which is not observed in the case of CO<sub>2</sub>, implying that the effect of Ni atoms on the adsorption of CO<sub>2</sub> is not much significant. This is because the d band of Ni atoms strongly interacts with the electronic states of SO<sub>2</sub> but does not interact with the electronic states of CO<sub>2</sub>. The critical role of the metal center of MOFs has been addressed in the literature. Nevertheless, this study shows that this role cannot be fulfilled if the d band of the metal center does not interact with the electronic states of the adsorbed gases. We also found that increased overlap in DOS causes more charge sharing and thus stronger binding of the gas to MOF. The specific interaction between SO<sub>2</sub> and Ni<sup>2+</sup> is unexpected since the metal ions in secondary building units of MOFs such as M(bdc)(ted)<sub>0.5</sub> (M is a transition metal) usually do not interact strongly with guest molecules because they are fully saturated and screened. Thus, this study presents an interesting finding, which explains the experimental result.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

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