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NO adsorption and reaction on single crystal rutile TiO₂(110) surfaces studied by UHV-FTIRS

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Abstract

The adsorption and reaction of NO on both the oxidized and reduced single crystal rutile TiO₂(110) surfaces were studied in a UHV-FTIRS system at low temperature. The monodentate adsorption configuration of the cis-(NO)₂ dimer at bridge oxygen vacancy (Vo) sites was detected for the first time on reduced TiO₂(110) surfaces. By the aid of (NO)₂ dimer adsorption anisotropy, the bidentate configuration of the cis-(NO)₂ dimer on fivefold coordinated Ti_{5c}⁴⁺ cation sites was clearly confirmed. The (NO)₂ dimer converts to N₂O on Ti_{5c}⁴⁺ cation sites at higher NO dosage on both oxidized and reduced surfaces, rather than at Vo sites. The (NO)₂ → N₂O conversion is independent of the presence of Vo on TiO₂(110) surfaces. To explain the signs of absorption bands of the dimer monodentate configuration, the local optical constant at Vo sites was introduced.

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1. Introduction

Nitric oxide (NO) is one of the main components in the atmosphere pollution that contribute to acid rain and global warming. How to efficiently transform and remove NO is an important issue in atmospheric environmental protection.¹ Titanium dioxide (TiO₂), as one of the best known photo-catalysts for its excellent physical and chemical properties, has important applications in reduction of NO and has attracted considerable attention both in theory and in experiments. Studies on NO adsorption and reaction on TiO₂(110) surfaces will be helpful in both understanding the reaction mechanism and seeking the way to (photo)catalytically transform NO in the atmospheric pollution remediation.

The unpaired π^* electron leads NO free radicals to be highly reactive and volatile. During NO chemical transform reactions the (NO)₂ dimer usually forms as an intermediate. The adsorbed (NO)₂ dimer mode had already been found on metal and metal oxide surfaces.²⁻⁴ Kugler et al. and Millman et al., respectively, proved that such NO-in pairs form the cis-(NO)₂ dimer.^{5,6} Theoretical calculations about gas phase and adsorbed (NO)₂ dimer formation have also been performed.⁷⁻⁹ In the (NO)₂ dimer formation, the $2\pi^*$ orbitals with the unpaired electrons overlap, forming a weak σ bond. All these give rise to a complicated coordination chemistry of NO on surfaces.

Early in 1992, Boccuzzi et al. have shown that the powered TiO₂ samples can transform NO into N₂O especially in the reduced condition using Fourier transform infrared spectroscopy (FTIRS).¹⁰ Rusu and Yates also found later that the adsorbed NO on reduced TiO₂ powers forms N₂O molecule with increased NO dosage at 110 K.¹¹ Lu et al. found the N₂O formation at NO adsorption on single crystal TiO₂(110) surfaces, and suggested that the bridge oxygen vacancy (Vo) was involved in the NO \rightarrow N₂O conversion.¹² Sorescu et al. investigated NO adsorption on the defect-free TiO₂(110) surface by combining experimental and theoretical analysis. They found the intermediate (NO)₂ dimer formation and identified its symmetric bidentate adsorption configuration in the singlet state.¹³ A recent combined experimental and computational study suggested that the monodentate adsorption configuration of cis-(NO)₂ species adsorbed through an N-Ti bond is the most stable on the TiO₂(110) surface at very low coverage on the (110) facet-terminated TiO₂ nanoparticles.¹⁴ However, the effects of the surface bridge Vo on NO adsorption, reaction, and the dimer adsorption state are still inconclusive so far. This is attributed to the lack of the comparison experiments for the NO adsorption and reaction on both the oxidized

and reduced single crystal TiO₂(110) surfaces with irrefutable experimental evidences.

Recently, in a new-designed ultrahigh vacuum (UHV)-FTIRS system,¹⁵ we studied in detail NO adsorption and reaction on both oxidized and reduced rutile TiO₂(110) surfaces by using reflection-absorption infrared spectroscopy (RAIRS) at low temperature. By combining the RAIRS measurement principle and the molecular adsorption anisotropy, the conclusive evidences of Vo effect and the (NO)₂-dimer adsorption structures were obtained. NO adsorbs on the Ti_{5c}⁴⁺ sites in the cis-(NO)₂ dimer bidentate configuration, while at the Vo sites in a monodentate configuration. At higher NO dosage, (NO)₂ dimer converts to N₂O on the Ti_{5c}⁴⁺ sites rather than at Vo sites. The conversion is independent of Vo's presence on TiO₂(110) surfaces.

2. Experimental

The experiments were performed in a UHV-FTIRS combination system, which combines a state-of-the-art vacuum FTIR spectrometer (Bruker, VERTEX 80v) with an UHV system consisting of a load-lock, a distribution and a measurement chambers. The base pressure of the measurement chamber is about 2×10^{-10} mbar. The oxidized single crystal rutile TiO₂(110) surface was cleaned by several cycles of Ar ion sputtering (2.5 kV, 10 mA) and annealing to 800K in O₂ atmosphere of 5×10^{-7} mbar in the measurement chamber. The reduced surface was obtained by a controlled sputtering and then annealing to 800 K under UHV condition on the oxidized surface. The sample temperature can change from 100 K, cooled by flowing liquid nitrogen, to 1000 K, heated by electronic beam with a resistance wire located in the sample holder. The RAIRS measurements were performed with the unpolarized IR beam at a fixed incidence angle of 80°. The recorded data, the reflectivity difference, is defined as $\Delta R = R_0 - R_a$, where R_0 and R_a denote the reflectivities of the bare TiO₂(110) surface and the molecule-covered surface. The spectra were obtained with 2048 scans at a resolution of 4 cm⁻¹. For measuring anisotropy, two crystals with the same preparation procedure were introduced with the incident infrared light plane along the [001] and $[1\bar{1}0]$ azimuths, respectively. During measurement, the IR detector was cooled down by liquid nitrogen. The optical path inside the IR spectrometer and the space between the UHV chamber and the spectrometer were evacuated in order to avoid any unwanted IR absorption from gas phase species. The purity of NO used in experiments was 99.8%.

3. Results and discussion

3.1 Oxidized TiO₂(110) surface

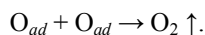
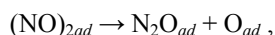
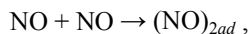
Fig. 1 shows the RAIR spectra of NO adsorbed on the oxidized rutile TiO₂(110) surface at 100 K with different NO dosage. During the measurement, the incidence plane is perpendicular to the [001] direction of the substrate. At 1.2 L dosage (1 L=1.33 × 10⁻⁶ mbar·s), two negative bands were observed at 1876 cm⁻¹ and 1746 cm⁻¹, respectively. With increasing NO dosage, their intensities gradually decrease and completely disappear at about 20 L of NO dosage. Meanwhile, another negative band at 2243 cm⁻¹ appears and increases in intensity with increasing NO dosage.

The 1876 cm⁻¹ and 1746 cm⁻¹ bands are assigned to the symmetric and asymmetric N-O stretching vibrations (ν_s and ν_{as}) of cis-(NO)₂ dimer.^{11, 16} This is in contrast to some cases such as CH₂, CH₃ groups in which the asymmetric stretch has a higher frequency than the symmetric stretch.¹⁷ This is probably due to the weak σ bond between the two NO free radicals within one (NO)₂ dimer. It was noted that the 1876 cm⁻¹ and 1746 cm⁻¹ bands always coexist even at very low NO dosage, and no obvious vibrational band of the isolated NO molecular was observed on the TiO₂(110) surface. One reason is that the dimers have already formed in gas phase,⁷ another reason is that the dimers formed very quickly when NO adsorbed on the surface. Such an adsorption mode of NO in pairs has already been found on many metal oxides.³ The 2243 cm⁻¹ band originates from the N-N stretching vibration of N₂O species.^{18, 19} Since adsorbed NO exists on TiO₂(110) first in (NO)₂ dimers, and then N₂O appears at the cost of (NO)₂ dimers, these sufficiently demonstrate the occurrence of the (NO)₂ → N₂O conversion. In addition, the fivefold coordinated Ti_{5c}⁴⁺ cation sites are the preferred sites for adsorbed (NO)₂ dimers and N₂O molecules as Lewis acid centers with N-bound on the TiO₂(110) surface.²⁰ Accordingly, we suggest that on the oxidized TiO₂(110) surface, NO adsorbs on Ti_{5c}⁴⁺ sites first in (NO)₂ dimer; with increasing NO dosage, the (NO)₂ dimer converts to N₂O due to one O atom removal.²¹ The 2190 cm⁻¹ band at low NO dosage comes from the co-adsorbed traces of CO on Ti_{5c}⁴⁺ sites from the background, which does not affect our conclusion because CO can be completely replaced at higher NO dosage.

At 20 L of NO dosage, both 1876 cm⁻¹ and 1746 cm⁻¹ bands completely disappear and the 2243 cm⁻¹ band reaches saturation, indicating that all the adsorbed (NO)₂ dimers have converted to

N₂O species. Since there are very few surface defects (V_o) on the oxidized surface, we conclude that the (NO)₂ → N₂O conversion is independent of the presence of V_o.

As the above discussions, the reaction of NO on oxidized TiO₂(110) surfaces evolves probably in the following way:



Here, the subscript *ad* denotes the adsorbed state.

To further identify the adsorption configuration of the adsorbates, their anisotropies on the oxidized surface were studied. The corresponding RAIR spectra are shown in Fig. 2. During the measurement, the incidence plane is along [001] direction. Interestingly, at low NO dosage (1 L), the vibrations of (NO)₂ dimers exhibit two absorption bands with opposite signs: negative ν_s band at 1876 cm⁻¹ and positive ν_{as} band at 1746 cm⁻¹. The different signs of (NO)₂ dimer vibration bands compared with those shown in Fig. 1 are attributed to the anisotropy of (NO)₂ dimer adsorption structure on the oxidized TiO₂(110) surface. With increasing NO dosage, both bands decrease and finally disappear; at the same time, the N₂O vibration band at 2243 cm⁻¹ appears and increases. This dependence of N₂O vibration band upon NO dosage is similar to that shown in Fig. 1, demonstrating that N₂O adsorption structure is isotropic along [001] and $[1\bar{1}0]$ directions on the TiO₂(110) surface.

Prior to elucidating the dimer configurations, the judgment principle was first introduced.²² On non-absorbing or weakly-absorbing surfaces such as semiconductor or insulator, both p-polarized and s-polarized lights interact with the transition dipole moments which arise from the vibrational modes of the adsorbed molecules. The interaction between the transition dipoles and the electric fields can give rise to absorption bands which are positive or negative, depending upon their relative alignment. When the transition dipole moment is certain, the relative alignment depends upon the angle of incidence and the polarization. At the angle higher than the Brewster angle (θ_B , the arctangent of the ratio of the refractive indices of the substrate and vacuum), the measured absorption bands are negative, positive, and negative due to the transition dipole moment aligned along E_{p_n} (vertical component of p-polarized light), E_{p_t} (parallel component of

p-polarized light) and E_s (s-polarized light) respectively.

In our measurement configuration, the incidence angle of the unpolarized infrared beam is fixed at 80° to the substrate surface normal, obviously higher than the θ_B of rutile $\text{TiO}_2(110)$ ($\sim 67^\circ$). When the incidence plane is along the $[001]$ direction, the s-polarized light is along the $[1\bar{1}0]$ direction, and the p-polarized light is nearly vertical to the (110) surface with a weak parallel component along the $[001]$ direction. According to the judgment principle introduced above, the strong positive ν_{as} band at 1746 cm^{-1} indicates that the ν_{as} vibration should have a stronger parallel component to the $[001]$ direction. Because ν_{as} is parallel to the N-N bond, as a result, the N-N bond of the $(\text{NO})_2$ dimer should be parallel to the $[001]$ direction on the $\text{TiO}_2(110)$ surface. This means that one $(\text{NO})_2$ dimer binds two adjacent Ti_{5c}^{4+} cations with two N atoms. For this bidentate adsorption structure, the cis- $(\text{NO})_2$ dimer plane is along the $[001]$ direction. Its schematic model is shown as State I in Fig. 4. This symmetric bidentate configuration of $(\text{NO})_2$ dimer in the singlet state is consistent to the result of the experimental and theoretical analysis.¹³ In this case, both ν_s and ν_{as} have no parallel components to the s-polarized light, and the ν_s vibration vertical to the surface exhibits a negative value. In contrast, when the incidence plane is along the $[1\bar{1}0]$ direction, the s-polarized light is along the $[001]$ direction, so that the ν_{as} vibration which is along the $[001]$ direction exhibits a negative band; On the other hand, the ν_s vibration vertical to the (110) surface is active to the vertical component of the p-polarized light (E_{p_n}) and exhibits also a negative value. These are all consistent with spectroscopic results as shown in Fig. 1.

In addition, the isotropic adsorption structure of N_2O along $[001]$ and $[1\bar{1}0]$ directions on the $\text{TiO}_2(110)$ surface indicates that the linear N_2O molecule adsorbs vertically on the Ti_{5c}^{4+} site with N-bound. The schematic model is shown as State II in Fig. 4. The vertical adsorption of N_2O also explains the fact that N_2O is stable for high NO dosage. Such adsorption geometry of N_2O on Ti_{5c}^{4+} sites is consistent with the theoretical calculations.^{14, 23}

3.2 Reduced $\text{TiO}_2(110)$ surface

To further elucidate the possible effect of Vo on the NO adsorption and reaction, NO adsorption on the reduced $\text{TiO}_2(110)$ surface at 100 K was also studied. The corresponding RAIR spectra with

different NO dosage are shown in Fig. 3. The measurement configuration is the same as that in Fig. 1, i.e., the incidence plane is perpendicular to the [001] direction. Strangely, for all the NO dosages, both the 1878 cm^{-1} and 1745 cm^{-1} bands exhibit positive values. Furthermore, with increasing NO dosage, both band intensities increase. Meanwhile, the 2243 cm^{-1} band exhibits the same dependence upon the NO dosage as that on the oxidized surface. At saturation, the 2243 cm^{-1} band intensity is also the same as that on the oxidized surface. This means that on the reduced surface, the amount of N_2O molecules at saturation should be the same as that on the oxidized surface. Since N_2O on the oxidized $\text{TiO}_2(110)$ surface are converted from all the $(\text{NO})_2$ dimers adsorbed on Ti_{5c}^{4+} cation sites, it is reasonable to suggest that N_2O on the reduced $\text{TiO}_2(110)$ surface are also converted from all the $(\text{NO})_2$ dimers adsorbed on the Ti_{5c}^{4+} cation sites. In addition, it is noticed that at saturation the N_2O stretch shows a lineshape, i.e., besides the negative band at 2243 cm^{-1} , a weak positive band with a small redshift was observed. This means that the N_2O is a little tilted due to interactions with nearby monodentate species. As described above, the positive weak band means that there's a small component along E_{pt} direction, i.e., the [001] direction. This is similar to that of CO or CO_2 adsorbed on $\text{TiO}_2(110)$ at higher coverage.^{24, 25}

The remained positive 1878 cm^{-1} and 1745 cm^{-1} bands for high NO dosage on the reduced surface are reasonably assigned also to the symmetric and asymmetric stretching modes of the $(\text{NO})_2$ dimer according to their vibrational frequencies. According to the different RAIR spectra for $(\text{NO})_2$ dimers on two differently treated surfaces, we ascribe these extra positive absorption bands to $(\text{NO})_2$ dimers adsorbed at Vo sites on reduced $\text{TiO}_2(110)$ surfaces. Since all the N_2O are converted from the dimers on Ti_{5c}^{4+} cation sites, we conclude that the $(\text{NO})_2$ dimers adsorbed at Vo sites won't convert to N_2O even for higher NO dosage.

Considering that the parallel component of p-polarized light (E_p) is along the $[1\bar{1}0]$ direction, both ν_s and ν_{as} bands exhibit positive values simultaneously, indicating that both vibrations must have strong parallel components along the $[1\bar{1}0]$ direction. This means that the $(\text{NO})_2$ dimer adsorbs at the Vo site in a monodentate structure rather than in the bidentate adsorption structure.¹⁴ In this case, one N within $(\text{NO})_2$ dimer is bound with two adjacent Ti^{3+} cations, and the dimer plane is perpendicular to the [001] direction. The schematic mode is shown as State III in Fig. 4. This monodentate structure seems consistent with that on Ti_{5c}^{4+} sites at very low NO coverage by

calculations.¹⁴

Actually, only the monodentate configuration cannot sufficiently give rise to both strong positive bands, for which the local optical constant at Vo site should be taken into account. According to the formula described by Buchholz et al.,²⁶ we performed the simulation calculation of reflectivity difference (ΔR) for $(\text{NO})_2$ dimers adsorbed on Ti_{5c}^{4+} sites and at Vo sites, respectively. The IR light is not polarized and the ratio between s- to p- amplitude is 1:1. The calculated ΔR , as a function of the incidence angle for the p-polarized (including E_{p_n} and E_{p_t} components) and s-polarized light are respectively shown in Figs. 5a and 5b. The insets show their adsorption configurations. The calculated ΔR at incidence angle 80° just corresponds to the measured absorption bands, i.e., the positive ΔR corresponds to the positive absorption band of corresponding intensity, and vice versa. For the dimer bidentately adsorbed on Ti_{5c}^{4+} sites, when the incidence light is aligned perpendicular to $[001]$ direction, v_s couples E_{p_n} , and v_{as} couples E_s . As shown in Fig. 5a, both v_s and v_{as} bands are negative. This corresponds to the case shown in Fig. 1. When the incidence light is perpendicular to $[1\bar{1}0]$ direction, v_s couples E_{p_n} , and v_{as} couples E_{p_t} , therefore, the former is negative and the latter positive. This corresponds to the case in Fig. 2. For the dimer monodentately adsorbed at Vo sites, the N-N bond is tilted by about 45° away from the surface normal and the dimer plane is perpendicular to $[001]$ direction. When the incidence light is perpendicular to $[001]$ direction, both v_s and v_{as} couple both E_{p_n} and E_{p_t} , i.e., both v_s and v_{as} couple E_p . As shown in Fig. 5a, though both of v_s and v_{as} bands are positive, they are very weak. Therefore, at Vo sites, the optical constant of substrate is decreased to 1.9, compared with 2.4 on Ti_{5c}^{4+} sites.²¹ In this case, as shown in Fig. 5b, the negative ΔR_{p_n} along E_{p_n} component is completely canceled by the strong positive ΔR_{p_t} along the parallel E_{p_t} , and ΔR_p of both bands show stronger positive values. This is consistent with the result shown in Fig. 3.

As mentioned above, the $(\text{NO})_2 \rightarrow \text{N}_2\text{O}$ conversion takes place on the Ti_{5c}^{4+} cation sites for higher NO dosage. Because the dimer plane on Ti_{5c}^{4+} cation sites are along the Ti_{5c}^{4+} row direction, as shown in Fig. 4, that is, the dimers are distributed end-to-end. For densely distributed $(\text{NO})_2$ dimers, the distance between adjacent dimers is so small that their strong interaction gives rise to one N-O bond broken within one dimer, resulting in N_2O formation. As for the dimers adsorbed at Vo sites, on the one hand, most of the bridge Vo are point defects because of the repulsive

interaction between them in the same row.^{27,28} On the other hand, the dimer plane is perpendicular to the bridge oxygen row. Both factors lead to the adjacent dimer distance not small enough for the $(\text{NO})_2 \rightarrow \text{N}_2\text{O}$ conversion to occur at Vo sites. Another possible reason is that the monodentate $(\text{NO})_2$ dimers are more stable because of the extra electron charges around the Ti^{3+} cations adjacent to Vo. On Ti_{5c}^{4+} cation sites, however, we cannot rule out the possibility that the dimer bidentate adsorption transforms to the monodentate adsorption as an intermediate during the conversion.

It is noted in experiments that the Vo density on $\text{TiO}_2(110)$ is not decreased after the $(\text{NO})_2 \rightarrow \text{N}_2\text{O}$ conversion, which indicates that the removed O atoms during the conversion do not fill Vo, but form O_2 molecules and desorb from the substrate surface. This is consistent with the reaction evolution as we suggested above.

4. Conclusions

In summary, the adsorption and reaction of NO on rutile $\text{TiO}_2(110)$ surfaces were studied in detail by UHV-FTIRS at low temperature. NO adsorbs on $\text{TiO}_2(110)$ in cis- $(\text{NO})_2$ dimer state. The dimer monodentate configuration adsorbed at bridge Vo sites was detected in experiments for the first time. On both oxidized and reduced surfaces, $(\text{NO})_2$ dimer adsorbs on the fivefold coordinated Ti_{5c}^{4+} cation sites in the bidentate configuration, in which the dimer plane is along the [001] direction. At higher NO dosage, $(\text{NO})_2$ dimer converts to N_2O on Ti_{5c}^{4+} sites rather than at Vo sites. The $(\text{NO})_2 \rightarrow \text{N}_2\text{O}$ conversion is independent of Vo's presence, and Vo is not filled by the O atom removing from the $(\text{NO})_2$ dimer. The local optical constant at Vo sites was introduced to explain the positive absorption bands of the dimer monodentate configuration.

Acknowledgements

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Figure captions:

Fig. 1. RAIR spectra of NO adsorbed on the oxidized $\text{TiO}_2(110)$ surface at 100 K with different NO exposure. The incidence plane is perpendicular to $[001]$ direction.

Fig. 2. RAIR spectra of NO adsorbed on the oxidized $\text{TiO}_2(110)$ surface at 100 K with different NO exposure. The incidence plane is along $[001]$ direction.

Fig. 3. RAIR spectra of NO adsorbed on the reduced $\text{TiO}_2(110)$ surface at 100 K with different NO exposure. The incidence plane is perpendicular to $[001]$ direction.

Fig. 4. Schematic models of $(\text{NO})_2$ dimer and N_2O molecule adsorbed on the reduced $\text{TiO}_2(110)$ surface. Red or pink ball denotes O, grey ball Ti and green ball N.

Fig. 5. Calculated ΔR for $(\text{NO})_2$ dimer adsorbed on Ti_{5c}^{4+} sites (a) and at Vo sites (b) as a function of incidence angle for p-polarized and s-polarized light at 1746 or 1876 cm^{-1} . The following optical constants were used for two adsorption sites: (a) Ti_{5c}^{4+} sites: refractive index $n_3 = 2.4$, extinction coefficient $k_3 = 0$, (b) Vo sites: $n_3 = 1.9$, $k_3 = 0$. For the adsorbate layer on both sites, the following parameters were used: thickness $d_2 = 1.14 \text{ \AA}$, $n_2 = 1.5$, $k_2 = 0.3$.²¹ θ_B denotes the Brewster angle of $\text{TiO}_2(110)$ substrates.

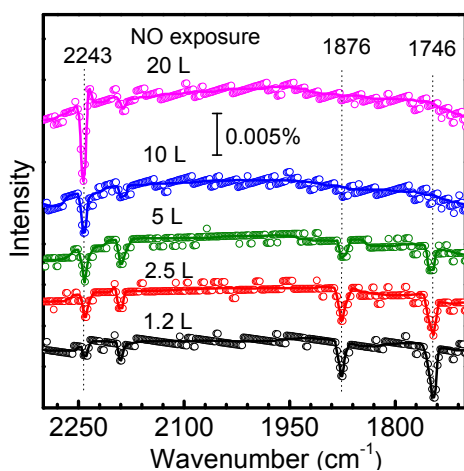


Fig. 1. RAIR spectra of NO adsorbed on the oxidized TiO₂(110) surface at 100K with different NO exposure. The incidence plane is perpendicular to [001] direction.

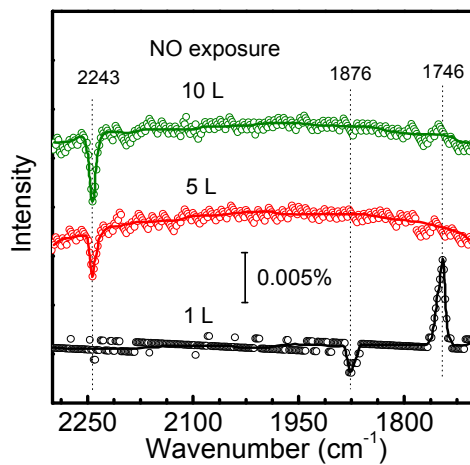


Fig. 2. RAIR spectra of NO adsorbed on the oxidized TiO₂(110) surface at 100K with different NO exposure. The incidence plane is along [001] direction.

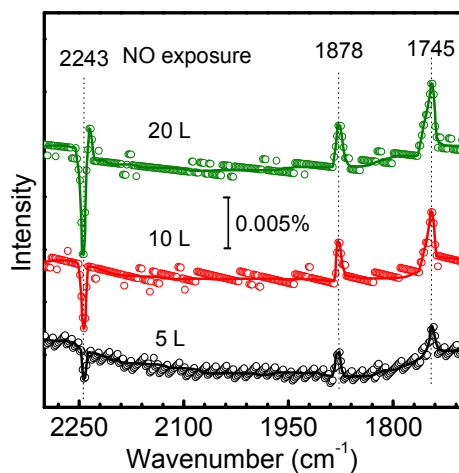


Fig. 3. RAIR spectra of NO adsorbed on the reduced TiO₂(110) surface at 100K with different NO exposure. The incidence plane is perpendicular to the [001] direction.

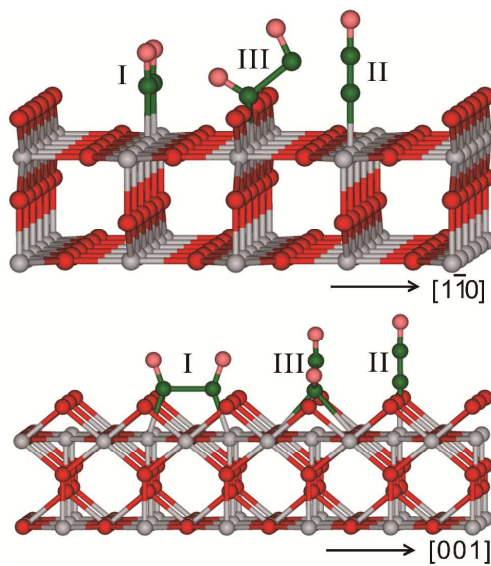


Fig. 4. Schematic models of (NO)₂ dimer and N₂O molecule adsorbed on the reduced TiO₂(110) surface. Red or pink ball denotes O, grey ball Ti and green ball N.

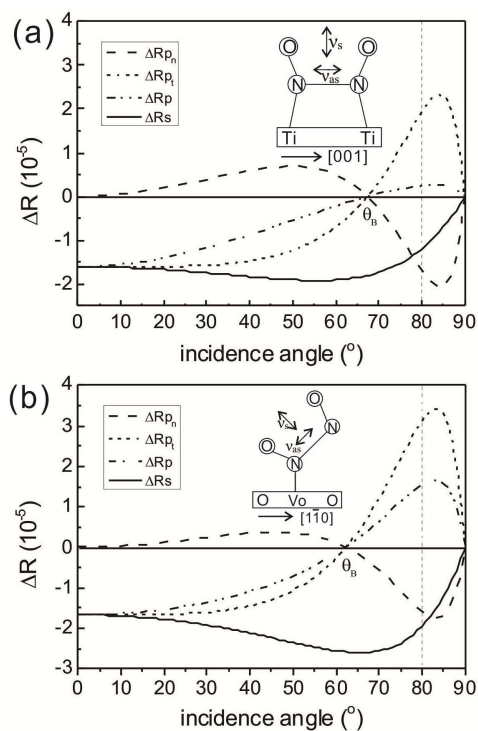


Fig. 5. Calculated ΔR for $(\text{NO})_2$ dimer adsorbed on Ti_{5c}^{4+} sites (a) and at Vo sites (b) as a function of incidence angle for p-polarized and s-polarized light at 1746 or 1876 cm^{-1} . The following optical constants were used for two adsorption sites: (a) Ti_{5c}^{4+} sites: refractive index $n_3 = 2.4$, extinction coefficient $k_3 = 0$, (b) Vo sites: $n_3 = 1.9$, $k_3 = 0$. For the adsorbate layer on both sites, the following parameters were used: thickness $d_2 = 1.14 \text{ \AA}$, $n_2 = 1.5$, $k_2 = 0.3$.²¹ θ_B denotes the Brewster angle of $\text{TiO}_2(110)$ substrates.