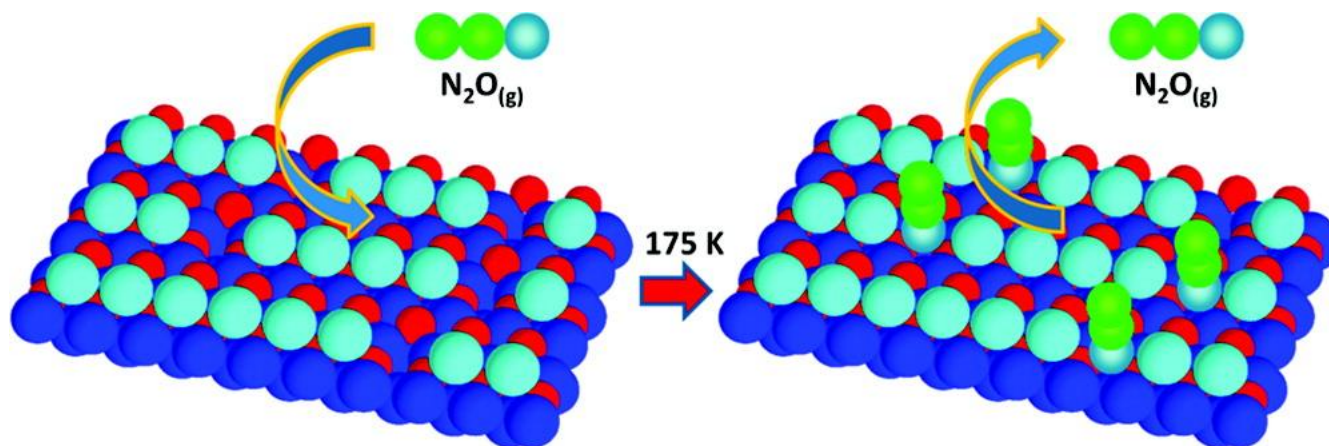


Unexpected Nondissociative Binding of N_2O on Oxygen Vacancies on a Rutile $\text{TiO}_2(110)-1 \times 1$

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Introduction:

Nitrogen oxides (NO_x) are commonly generated from the combustion of hydrocarbons in air, and they represent a major component in air pollution that can lead to acid rain and global warming.

In successive catalytic reduction of NO_x , the conversion of N_2O to N_2 becomes a rate-limiting step at the final stage and, therefore, has been studied on various oxides, such as TiO_2 , CeO_2 , ZrO_2 , $\text{BaO}/\text{Al}_2\text{O}_3$, and Fe_2O_3 . The results generally indicate the decomposition of the N_2O molecule, presumably at defects such as oxygen vacancy (V_{O}) sites.

A rutile $\text{TiO}_2(110)$ - 1×1 surface provides a well-characterized platform for studying the catalytic role of V_{O} 's, since they are easily prepared on the bridge-bonded oxygen rows (O_{b}) with controlled concentrations of up to 10% by sputtering and annealing up to 900 K in ultrahigh vacuum (UHV).

Numerous studies have revealed that V_{O} 's are the active sites for the dissociative adsorption of many oxygen-containing molecules, such as H_2O , O_2 , and alcohols. N_2O , which is the subject of this study, was also reported to dissociate in V_{O} 's yielding $\text{N}_2(\text{g})$ and O_{b} : $\text{N}_2\text{O}(\text{g}) + V_{\text{O}} \longrightarrow \text{N}_2(\text{g}) + \text{O}_{\text{b}}$.

The charge transfer from V_{O} to N_2O leading to N_2 and O_{b} has been proposed on the basis of electron energy loss spectroscopy (EELS) and second-harmonic generation (SHG) measurements.

TPD has been performed by Henderson *et al.*, which suggested that there are two channels for N₂O dissociation over V_O sites.

DFT calculations by Oviedo *et al.* proposed that the N₂O dissociation on V_O's has, at most, a very small energy barrier.

Despite a series of reports suggesting dissociation of N₂O over VO's, some of the reported experimental findings are inconsistent with the catalytic reduction of N₂O. If the V_O-bound N₂O molecules are consumed to form N₂, the amount of N₂O desorbed should be smaller than that totally adsorbed.

Contrary to the expectation, the results from Henderson *et al.* indicate that there is no change in the number of N₂O molecules between adsorption and desorption. However, other evidence suggests V_O annihilation and oxygen adatom accumulation on Ti⁴⁺ sites after N₂O TPD, indicating dissociation of N₂O.

In this paper, they re-examined the interaction of N₂O with V_O's on a reduced rutile TiO₂(110)-1 × 1 surface using a quantitative TPD measurement combined with a flux-calibrated molecular beam apparatus. And the results show that N₂O does not dissociate over V_O's on TiO₂(110) under typical thermal reaction conditions in a UHV chamber.

Experimental Details:

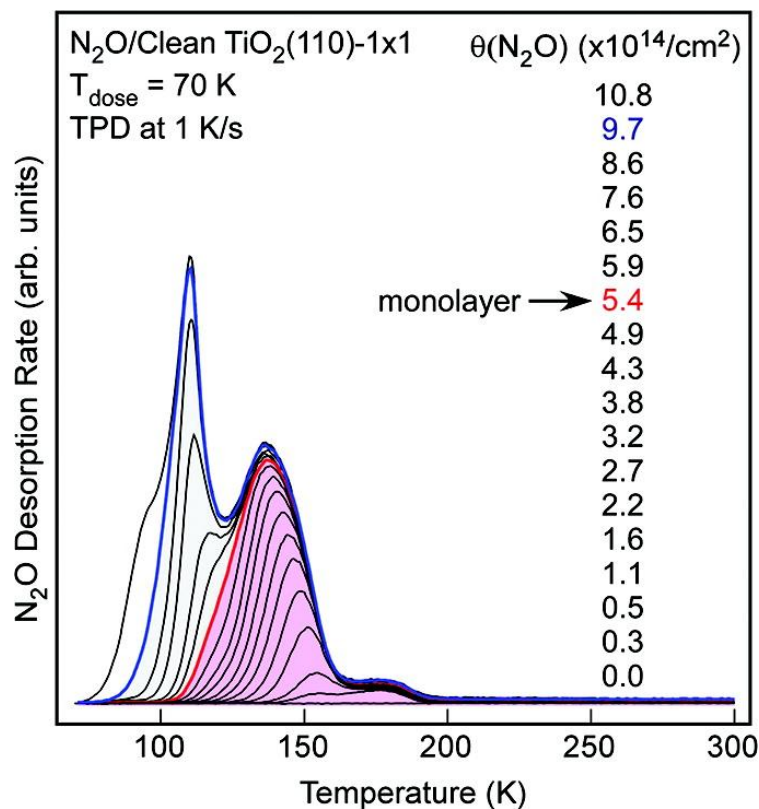
The experiments were performed in a UHV molecular beam surface scattering apparatus and the surface temperature of the TiO₂ (110) substrate could be controlled in the range of 60-1000 K.

A typical slightly reduced rutile TiO₂(110)-11 surface, r-TiO₂(110), with an atomically well-ordered arrangement of Ti⁴⁺ rows and bridge-bonded oxygen rows was obtained by repeated cycles of Ne⁺-sputtering at 300 K and annealing to 850 K.

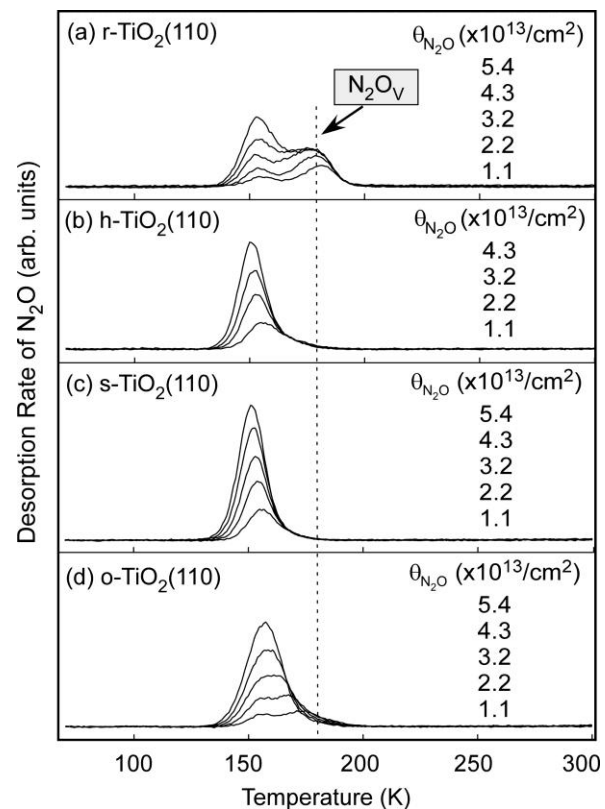
H₂O TPD measurements were used to measure the surface structural order and the V_O concentration from the integrated area of the recombinative H₂O desorption peak at 500 K.

Hydroxylated TiO₂(110), h-TiO₂(110), was prepared by dosing 2 ML of H₂O at 70 K, followed by annealing to 400 K to desorb H₂O molecularly bound on the Ti⁴⁺ sites, leaving only hydroxyls, HO_b's, formed on the O_b rows via H₂O dissociation on V_O's: $\text{H}_2\text{O} + \text{V}_\text{O} + \text{O}_\text{b} \longrightarrow 2\text{HO}_\text{b}$. The h-TiO₂(110) was further exposed to 10 Langmuir of O₂ at 300 K to dehydroxylate the surface ($4\text{HO}_\text{b} + \text{O}_2 \longrightarrow 2\text{H}_2\text{O} + 4\text{O}_\text{b}$), thereby producing a V_O-free TiO₂(110), s-TiO₂(110). Reduced TiO₂(110) was also dosed with O₂ at 70 K to prepare a V_O-free TiO₂(110) surface with oxygen adatoms on Ti⁴⁺ sites, o-TiO₂(110).

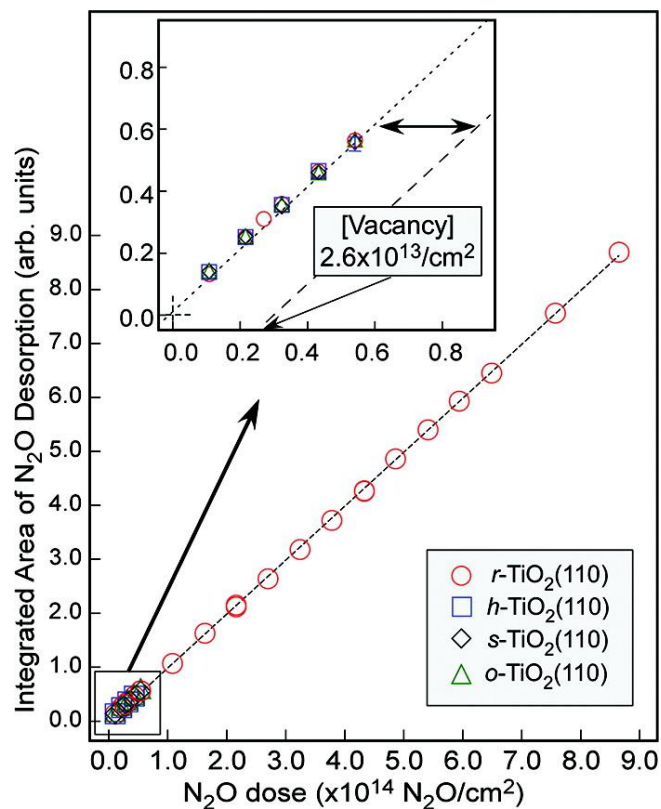
N₂O dosing was performed using a quasieffusive molecular beam directed onto the TiO₂ substrate at 70 K. The absolute flux of N₂O in the beam was measured 1.1×10^{14} N₂O/cm² s. After N₂O dosing, TPD spectra were taken using a quadrupole mass spectrometer at a heating rate of 1 K/s.



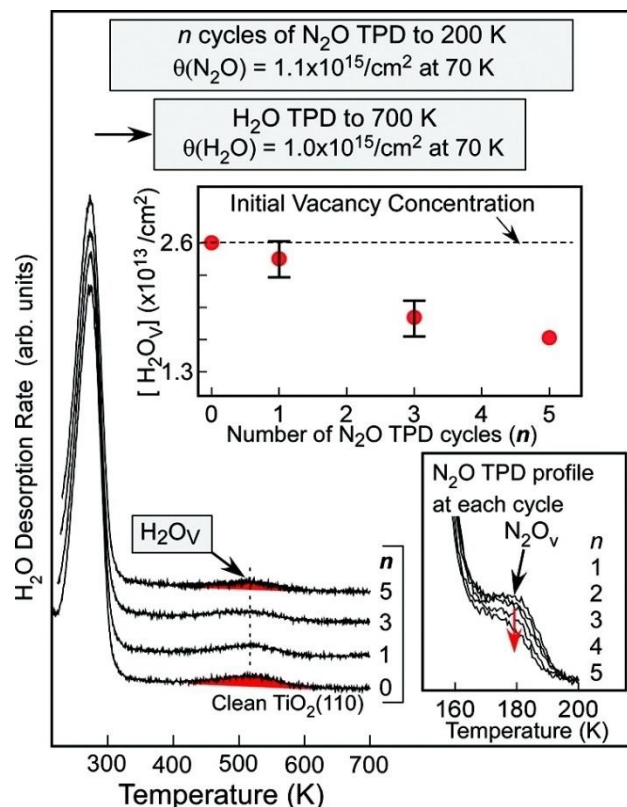
N_2O TPD ($m/e = 44$) spectra from N_2O dosed at 70 K on a partially reduced rutile $\text{TiO}_2(110)\text{-}1 \times 1$ with an oxygen vacancy (VO) concentration of 5%. The saturation coverage of N_2O on Ti^{4+} rows is $5.4 \times 10^{14}/\text{cm}^2$.



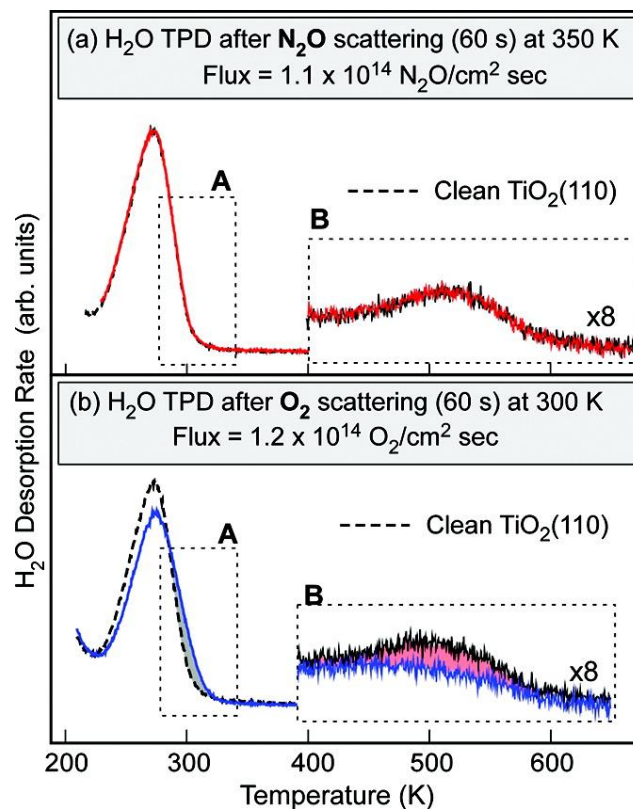
N_2O TPD ($m/e = 44$) spectra from N_2O dosed on differently prepared $TiO_2(110)$ surfaces. The correlation between the N_2O peak at 175 K and VO's can be established on the basis of its depletion on hydroxylated, stoichiometric, and oxidized $TiO_2(110)$ surfaces (h-, s-, and o- $TiO_2(110)$).



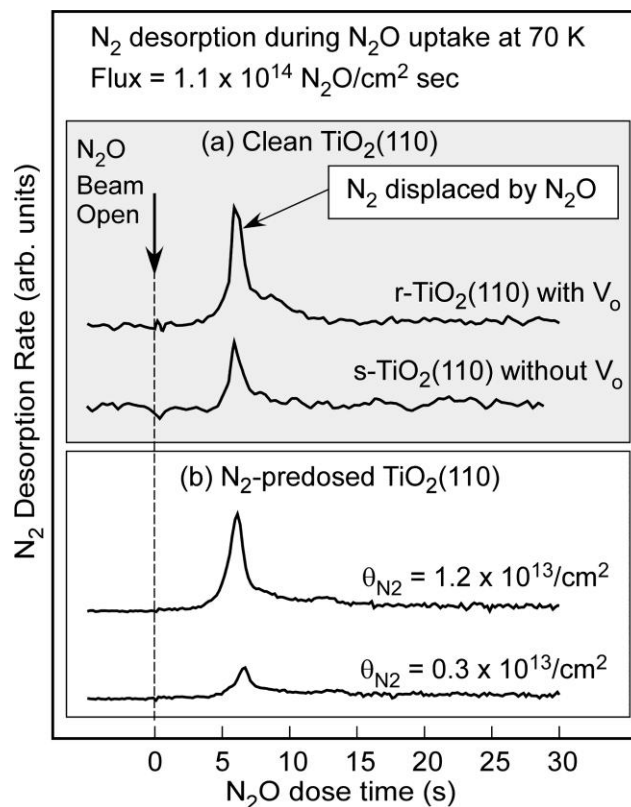
Integrated area of N₂O desorption as a function of N₂O dose at 70 K. The inset shows an expanded view of the low N₂O dose regime.



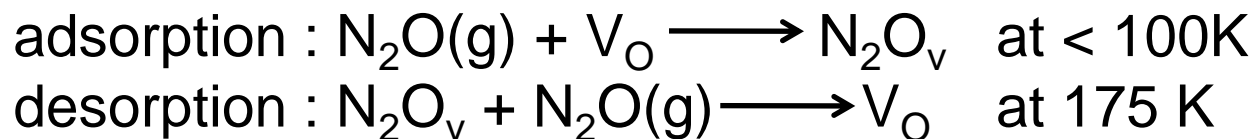
H_2O TPD ($m/e = 18$) spectra obtained after n N_2O adsorption/desorption cycles. The H_2O TPD's were obtained after an H_2O dose of $1 \times 10^{15} \text{ H}_2\text{O}/\text{cm}^2$ at 70 K using a heating rate of 1 K/s. The integrated areas of the V_O -related H_2O peak (H_2O_v) at 500 K are plotted in the top inset. The N_2O adsorption/desorption cycles were taken only up to 200 K after dosing $1.1 \times 10^{15} \text{ N}_2\text{O}/\text{cm}^2$ at 70 K. The corresponding changes in the V_O -related peak at 175 K are shown in the lower inset.



H₂O TPD ($m/e = 18$) spectra before and after (a) N₂O (top) and (b) O₂ (bottom) scattering at 350 K, respectively. The highlighted regions A (~ 300 K) and B (~ 500 K) in the H₂O desorption profiles indicate the absence (presence) of changes after the N₂O (O₂) dose.



N₂ desorption ($m/e = 28$) profiles during N₂O scattering at 70 K from (a) clean and (b) N₂ predosed TiO₂(110) surfaces.



Conclusions:

They examined the adsorption, dissociation, and desorption of N_2O on oxygen vacancies of the $\text{TiO}_2(110)\text{-}1 \times 1$ surface using a combination of molecular beam dosing and TPD.

The results clearly indicate that the adsorption and desorption of N_2O on the $\text{TiO}_2(110)$ surface occur molecularly without any dissociation. Only a slightly higher binding energy of VO-bound N_2O is observed (desorption temperature of 175 K), in comparison with the Ti-bound N_2O (desorption temperature of 150 K).

TPD results do not provide any evidence for the difference in the binding energies between the O-end- and N-end-bound N_2O on TiO_2 .

Repulsive interactions between N_2O molecules adsorbed on the Ti^{4+} sites represent the likely origin of a gradual shift of the monolayer N_2O TPD peak from 150 to 135 K with increasing N_2O coverages.

Further possibilities:

Same experiment can be carried out in presence of UV light that may lead to dissociation of N_2O .

Photocatalytic oxidation of CO to CO_2 in presence N_2O as an oxidant on TiO_2 surface can be studied.

Thank You