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**Title**
ISOTOPE EXCHANGE STUDIES OF THE OXIDATION AND REDUCTION OF SrTi03 SINGLE CRYSTAL SURFACES BY WATER AND HYDROGEN

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**Publication Date**
1980-02-01

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## UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

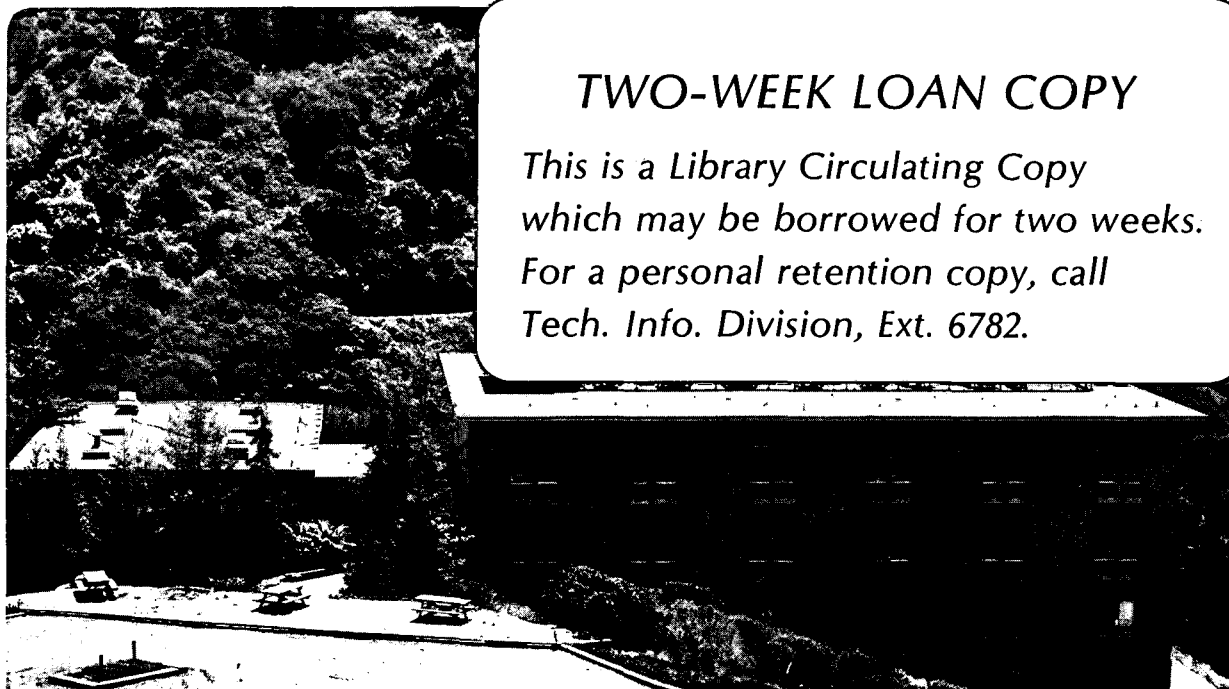ISOTOPE EXCHANGE STUDIES OF THE OXIDATION AND REDUCTION OF $SrTiO_3$ SINGLE CRYSTAL SURFACES BY WATER AND HYDROGEN

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February 1980

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# ISOTOPE EXCHANGE STUDIES OF THE OXIDATION AND REDUCTION OF

## SrTiO₃ SINGLE CRYSTAL SURFACES BY WATER AND HYDROGEN

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## Abstract

Thermal desorption studies of chemisorbed $D_2$ and $D_2O$ on a reduced SrTiO₃(111) surface reveal that $D_2$ causes the reduction of the crystal, whereas $D_2O$ causes its oxidation. Thermal desorption of $H_2^{18}O$ indicates that there is a 15% exchange between the oxygen in the adsorbed water molecules and the lattice oxygen.

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## Introduction

Strontium titanate is capable of catlyzing the sustained photodecomposition of water into hydrogen and oxygen when illuminated by band gap radiation (3·2 eV) in the photoelectrochemical cell without any applied external potential.[1] While several papers dealing with various surface properties of $SrTiO_3$ single crystals and other titanium oxides have been published[2-6] an understanding of the electronic and structural properties of the clean surfaces and their interaction with $H_2$, $H_2O$, and $O_2$ is still far from complete. In this paper we report on the thermal desorption of adsorbed $D_2O$, $D_2$, and $H_2{}^{18}O$ from a $SrTiO_3(111)$ surface. Mass balance arguments enable us to concude that in the case of $D_2O$ adsorption, a net oxidation of the crystal occurs, whereas in the case of $D_2$ adsorption there is a net reduction. Experiments with $H_2{}^{18}O$ allow us to quantitatively determine the amount of oxygen exchanged between the adsorbed water and lattice oxygen during the thermal desorption run. It is found that 15% of the water molecules desorbed from a $SrTiO_3(111)$ surface previously exposed to $H_2{}^{18}O$ water vapor contain ${}^{16}O$ from the crystal lattice.

## Experimental

$SrTiO_3$ single crystals supplied by National Lead were used in this study. These are of the (111) orientation (as determined by Laue back X ray diffraction) and before inserting into the vacuum system they were reduced in a $H_2$ furnace for several hours at 700°C, resulting in black coloration. The UHV system has been described elsewhere.[4,5] The base pressure was in the low $10^{-10}$ Torr range. The mass spectrometer was a UTI model 100c. $H_2{}^{18}O$ was supplied by Monsanto Company. The crystal was supported by a tungsten wire and heated radiatively by a tungsten filament from the back. The crystal temperature was measured with a chromel-alumel thermocouple in mechanical

contact with the crystal surface. The average crystal heating rate was ∿15 K
sec$^{-1}$ during the thermal desorption experiments. Before gas exposure the crystal
surface was cleaned by Ar ion sputtering for about five minutes, followed by
a brief annealing to ∿650°C and subsequent cooling to room temperature. As a
result of this treatment the surface was clean and reduced as monitored by
AES and UPS.[7]

## Results and Discussion

After chemisorptions of $D_2$ or $D_2O$ on the clean and reduced
$SrTiO_3$(111) surface, the thermally desorbed molecules that could be
detected were L and $D_2O$. Figure 1 (upper curve) shows the thermal desorption
trace of $D_2O$ after 1 L (1L=1x10$^{-6}$ Torr x sec) of $D_2O$ exposure of the clean
surface. It consists of a broad peak with a maximum at 285°C and it is asym-
metric. The desorption peak on the low temperature side is about 1.6 times
larger than that on the high temperature side. The relatively high temperature
of the peak maximum is indicative of the presence of hydroxyl species on the
surface that forms during $D_2O$ adsorption in agreement with previous reports on
$SrTiO_3$ and $TiO_2$.[4,7-9] Some molecular water adsorption and subsequent desorption
is also indicated by the broad low temperature shoulder of the thermal desorption
trace. The second curve in Fig.1 corresponds to the thermal desorption of $D_2$
after 1 L $D_2O$ exposure. It is a rather sharp peak at 418°C. The desorption
of $D_2$ indicates that oxygen was left behind at the surface of the oxide.

Figure 2 shows the thermal desorption spectra of $D_2O$ (upper curve)
and $D_2$ (lower curve) after an exposure of the clean surface to 3 L of $D_2$. The
$D_2O$ desorption trace is symmetric and the temperature of the peak maximum is
the same as that observed during the thermal desorption of $D_2O$ after $D_2O$ adsorption
within the experimental error (∿±10°C). The desorption trace of $D_2$ also has a

peak at the same temperature which was exhibited following $D_2O$ adsorption. The presence of desorbed $D_2O$ after a $D_2$ exposure indicates that oxygen is removed from the crystal.

The relationship between the ratio of the areas under $D_2$ and $D_2O$ desorption traces and the relative number of $D_2$ and $D_2O$ desorbed molecules is given by[10,11]

$$\frac{N_{D_2}}{N_{D_2O}} = C \frac{S_{D_2}}{S_{D_2O}} \qquad \frac{\text{Area under } D_2 \text{ peak}}{\text{Area under } D_2O \text{ peak}}$$

where $N_{D_2}$ and $N_{D_2O}$ are the total number of desorbed molecules, and $S_{D_2}$ and $S_{D_2O}$ are the pumping speeds for the two molecules. The ratio $(S_{D_2}/S_{D_2O})$ has been measured and is approximately 13.5. The proportionality constant C relates the ratio of the partial pressures of $D_2$ and $D_2O$ to the ratio of the intensities of mass spectrometer signals. It meainly depends on the cracking patterns and on the relative ionization efficiencies of $D_2$ and $D_2O$.[12] We obtained a value for C of 0.7. The ratio between the areas under the $D_2$ and $D_2O$ mass spectral curves in Fig. 2 is 0·6 which corresponds to a $N_{D_2}/N_{D_2O}$ ratio of 5·6.

We may write $D_2(ads) \longrightarrow (1-x)D_2(g)+xD_2O(g)$ where the left part refers to the amount of adsorbed deuterium due to 3 L exposure, the right part refers to desorbed gases, and x indicates the proportion of $D_2$ that reacts with the crystal giving $D_2O$ in the gas phase. We can calculate x from $5·6 = \frac{1-x}{x}$ obtaining x=0.15. Thus 15% of adsorbed $D_2$ molecules react with the crystal yielding $D_2O$. We can represent this reaction as $D_2(ads) + O \text{ crystal} = D_2O(g)$. This equation is obtained on the basis of mass balance arguments and it indicates that there is a reduction of the crystal as a consequence of the thermal desorption experiment.

Similar analysis for the $D_2O$ adsorption experiment reveals that the

the ratio of the areas under the $D_2$ and $D_2O$ peaks in Fig.1 is 0·3 which

corresponds to $(^ND_2/^ND_2O)=2.8$. Thus we may write $D_2O(ads)=(1-x)D_2O(g)+$

$x(D_2(g)+O_{crystal})$ where (1-x) indicates the fraction of $D_2O$ that does not

react and x is the fraction that reacts giving $D_2$ in the gas phase and leads

to oxygen incorporation in the crystal lattice. We can calculate x from

$2·8 = \frac{x}{1-x}$ obtaining x=0.74. Thus the reaction leading to an oxidation of the

crystal by adsorbed $D_2O$ is about five times more probable than the reduction

of the crystal by adsorbed deuterium. This is consistent with our observations

using UPS and XPS which reveal that the crystal surface is very much reduced,

containing about one monolayer of $Ti^{3+}$ ions.[7] UPS measurements show a

decrease on the concentration of $Ti^{3+}$ surface ions after the thermal desorption

experiment compared with the initial concentration before the $D_2O$ exposure. It

should be pointed out that the above model of the crystal oxidation by water

is much too simple. It is likely that after thermal desorption of adsorbed

$D_2O$, OD species in addition to atomic oxygen were left behind at the oxide surface.

In order to determine if significant exchange between the oxygen in

the adsorbed water and the lattice oxygen occurs during thermal desorption,

adsorption of $H_2^{18}O$ was also performed. The measured purity of the $H_2^{18}O$ vapor

was 87%. Figure 3 shows the thermal desorption spectra of water after 1 L

exposure of $H_2^{18}O$ on the clean and reduced surface. The tem-

peratures of the peaks are different by ∿30°C, indicating a difference in acti-

vation energies for desorption between the two species.

After a pure $H_2^{18}O$ adsorption, the thermally desorbed water in the

gas phase will consist of $H_2^{18}O$ and $H_2^{16}O$, their ratio depending on the amount

of exchange. We may define a parameter E as the ratio of $H_2^{16}O$ to the total

number of water molecules $(H_2^{16}O + H_2^{18}O)$ thermally desorbed from the crystal

after exposure to pure $H_2^{18}O$. The hypothetical value E=1 would mean that after a pure $H_2^{18}O$ adsorption the water leaving the surface due to a thermal desorption experiment would be $H_2^{16}O$ only. We can calculate E from the experimental ratio between the areas under the two curves in Fig.3 taking into account the actual purity of the $H_2^{18}O$ used. The ratio between the areas under $H_2^{16}O$ and $H_2^{18}O$ desorption traces in Fig.3 is 0·36 which is practically identical to the $N_{H_2^{16}O}/N_{H_2^{18}O}$ ratio. After pure $H_2^{18}O$ exposure, the ratio between the thermally desorbed water molecules $N_{H_2^{16}O}/N_{H_2^{18}O}$ is given by $\frac{E}{1-E}$. For the actual $H_2^{18}O$ purity (13% of $H_2^{16}O$) we must write $\frac{13+87E}{87(1-E)}=0.36$ that leads to E=0.15. This indicates that after water adsorption on the clean and reduced $SrTiO_3(111)$ surface, 15% of the water molecules desorbed due to a thermal desorption experiment originating from the interaction of lattice oxygen with hydrogen.

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## Figure Captions

Figure 1  Thermal desorption traces for $D_2O$ (upper curve) and $D_2$ (lower curve) after 1 L $D_2O$ exposure on the clean and reduced $SrTiO_3$(111) crystal face.

Figure 2  Thermal desorption traces for $D_2O$ (upper curve) and $D_2$ (lower curve) after 3 L $D_2$ exposure on the clean and reduced $SrTiO_3$(111) crystal face.

Figure 3  Thermal desorption traces for $H_2^{18}O$ (upper curve) and $H_2^{16}O$ (lower curve) after 1 L of $H_2^{18}O$ (purity 87%) exposure.
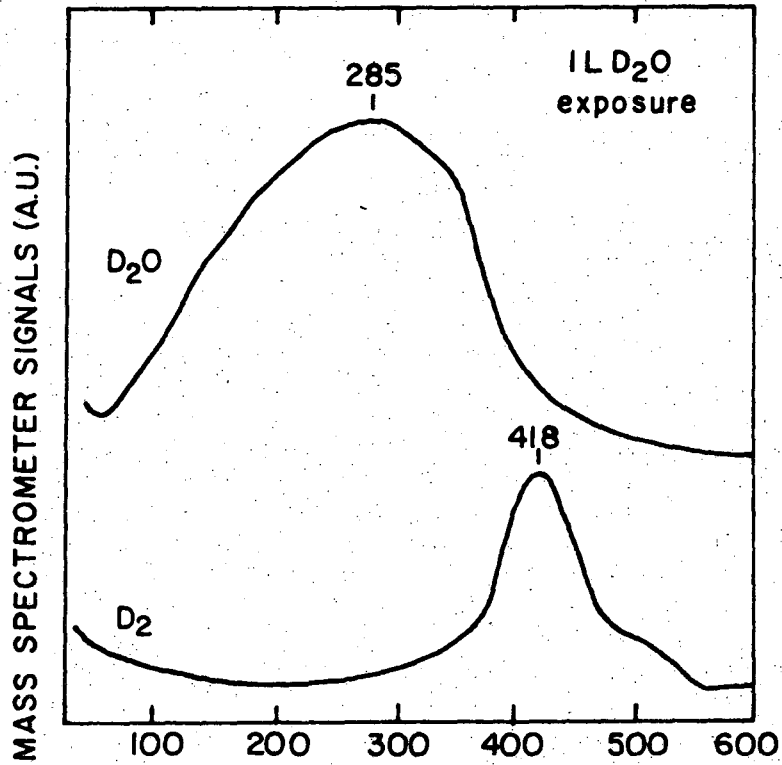
Fig. 1

Fig. 2

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Fig. 3

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