PHOTO-INDUCED REACTIONS OF GASES ADSORBED ONTO SEMICONDUCTOR SURFACES

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ONTOSTEMICONDUCTOR SURFACES

Roger Gladwin Carr
(Ph.D. thesis)

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PHOTO-INDUCED REACTIONS OF GASES ADSORBED ONTO SEMICONDUCTOR SURFACES

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ABSTRACT

Photodissociation of water adsorbed from the gas phase onto the platinized surface of SrTiO₃ single crystals is shown to occur. In the temperature range from 375-475 K and in the presence of several atmospheres of water vapor, several thousands of monolayers of hydrogen produced from photodissociation of water were detected. Therefore the surface of SrTiO₃ participated in the reaction as a catalyst, but not as a reactant.

Attempts were made to synthesize methane from carbon dioxide and hydrogen, the latter being produced from photodissociation of water as above. The presence of carbon dioxide did not interfere with hydrogen production, but catalysts which promote methane synthesis were found to promote the back conversion of methane and water into hydrogen and carbon dioxide.

Auger electron spectroscopy, ultraviolet photoelectron spectroscopy, and thermal desorption spectroscopy were used to examine the surfaces and adsorbates used in the preceding experiments. It was found that SrTiO₃ which had no detectable Ti³⁺ ions on the surface would adsorb water under the conditions of the earlier experiments.
Hydroxylation of the surface of \( \text{SrTiO}_3 \) was shown to increase its ability to adsorb carbon dioxide, and to promote the oxidation of carbon monoxide.
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CHAPTER 1
INTRODUCTION

A. Introduction and History

This chapter is an introduction to the following chapters and an explanation of the experiments to be described. The strategy of the experiments was to establish the existence of new surface effects and then to attempt to analyze them. The second chapter is a description of a new water dissociation reaction on a semiconductor surface. The third chapter is a description of attempts to use the water dissociation reaction as a step in hydrocarbon synthesis. The last chapter is a description of analytical experiments done with ultrahigh vacuum techniques to understand the exploratory experiments.

This work was done in order to gain more understanding of the mechanism of photodissociation of molecules on semiconductor surfaces. Experiments in this field were first done in aqueous electrolyte photoelectrochemical cells.\textsuperscript{1-4} The work described here is an extension of earlier work where instead of aqueous electrolyte, I used water adsorbed onto the semiconductor from the gas phase.\textsuperscript{5} The essential new finding was that water adsorbed this way was dissociated when the semiconductor was illuminated with band-gap light, and that this process was catalytic in the sense that the surface was chemically active, but was not consumed as a reactant.

Ten years ago, Fujishima and Honda found that water could be dissociated into molecular hydrogen and oxygen in an electrochemical cell in which ultraviolet light was allowed to strike a TiO\textsubscript{2} surface.\textsuperscript{6} Oxygen was evolved at the semiconductor anode. A wire connected the
anode to a platinum cathode, where hydrogen was evolved. The economic appeal of generating hydrogen from sunlight and water has since led to research with the goal of making the technical efficient enough to be practical. There are two major causes of inefficiency at present. One is that only a small portion of the solar spectrum is absorbed in materials which are stable enough to resist corrosion in electrolytes. The other is that only a portion of the light which is absorbed causes the dissociation of water. The nature of the semiconductor, particularly its surface properties, determines the latter effect, and it is this problem I propose to examine in the present work.

My approach was to study a SrTiO$_3$ as a model semiconductor electrode, and to connect the photochemical properties with surface properties which could be studied using ultrahigh vacuum electron spectroscopy techniques. Electrochemical techniques such as cyclic voltammetry, are used to study the properties of semiconductor electrodes in electrochemical cells. These techniques reveal little about the molecular processes at the surface except for their thermodynamics. It is technically difficult to remove an electrode from an electrochemical cell and subject it to ultrahigh vacuum analytical techniques. One difficulty is contamination of the surface by the electrolyte. I proposed that water adsorbed from the gas phase onto an illuminated semiconductor surface might be dissociated. If this happened, it would be relatively simple to examine the surface before and after exposure to water.

A brief description of this experiment is necessary for the introductory chapter; see Chapter 2 for the full discussion. A single
crystal of SrTiO₃ is coated partially with evaporated platinum. It is placed in a reaction chamber which is filled with a few atmospheres of water vapor at temperatures between 375 K and 475 K. Ultraviolet light strikes the platinized face of the crystal, and causes water adsorbed onto it to be dissociated. The platinum acts as a catalyst for recombination and desorption of hydrogen.

Both the liquid and gas phase experiments have several subsystems: the semiconductor bulk, the semiconductor surface, the adsorbates on that surface, and the metal. In the remainder of this chapter I shall discuss the physics and chemistry of each subsystem.

B. Electrochemistry

In the experiment of Fujishima and Honda, they allowed ultraviolet light to strike n-type TiO₂ in an acidic electrolyte. See Figure 1-1. They surmised that electron-hole pairs created by light in the semiconductor were separated so that holes reacted with water at the surface of the semiconductor anode. Electrons travelled through the bulk of the semiconductor to the face opposite the light, entered a wire and flowed to a platinum cathode, where they reacted with water. The anode reaction is \( 2p^+ + H_2O = 1/2 O_2 + 2H^+ \) in acidic electrolyte, and the cathode reaction is \( 2e^- + 2H^+ = H_2 \). The electrolyte is acting as an ionic conductor in that \( H^+ \) flows from anode to cathode. The role of electron-hole pairs was inferred from measurements of electrical current in the circuit connecting anode to cathode, and from the fact that bandgap radiation (above 3.0 eV) was necessary to produce any photocurrent. It was necessary in the case of TiO₂ to provide a small additional bias potential in the form of a DC voltage supply in the
Fig. 1-1

Electrolyte

TiO$_2$ anode

UV light

O$_2$

Pt cathode

H$_2$

H$^+$

e$^-$
external circuit, or a salt bridge between anode electrolyte and cathode electrolyte, which were at different pH. The electrochemical potential necessary to dissociate liquid water at room temperature is 1.23 V, and about 0.25 V bias was needed to achieve appreciable rates.

It is appropriate at this point to present a brief discussion of relevant electrochemistry from a physicist's point of view. I shall use the solid state physics convention that energy levels are referred to the vacuum level at 0 V, and that other levels in solution are negative. It is usual in electrochemistry to refer all energy levels to an arbitrary standard, normally the energy level of the $H^+$ ion. However, it has been found recently that the $H^+$ level can be assigned the absolute value of $-4.6 \pm 0.1$ V. These measurements refer to the $H^+$ ion in an aqueous solution of pH 0; if the solution has greater pH value, the energy level of the $H^+$ ion shifts by $-0.059$ V/pH.

Platinum is used as a cathode material because it does not undergo irreversible reactions with the electrolyte and because it will chemisorb hydrogen. These properties allow it to discharge electrons to the $H^+$ ion with negligible overvoltage at low current densities at any pH. Also the oxide semiconductors energy levels will shift with pH of an electrolyte in which they are immersed at $-0.059$ V/pH. Even if a semiconductor did not shift according to this rule, or shift very quickly, it would be forced to if attached to a platinum cathode through an ohmic contact.

In general a potential drop will appear across a layer of adsorbates on the semiconductor called the Helmholtz layer. This potential drop is given for simple cases by: $V_H = 0.059(pH_{zzp} - pH)$ where
\( \text{pH}_{\text{pzzp}} \) (the point of zero zeta potential) is the pH of a solution for which the Helmholz layer is charge balanced so that there is no potential difference across it. \(^{12}\) For \( \text{TiO}_2 \) \( \text{pH}_{\text{pzzp}} = 6.0 \); for \( \text{SrTiO}_3 \) \( \text{pH}_{\text{pzzp}} = 8.2 \). \(^{13}\) Thus at pH 0 \( V_H \) will be positive for both, at pH 14 it will be negative for both. See figure 1-2. For this reason it makes sense to use a basic electrolyte so as to allow the contact potential difference between the electrolyte and the semiconductor to create the maximum band bending inside the semiconductor. The greater the band bending, the greater the efficiency of electron-hole separation. The Helmholz layer is so thin that tunnelling across it can occur easily.

The energy level of the \( \text{H}^+ (\text{H}_2\text{O}^+) \) ion is the potential \( V = -\Delta G/nF \) of the half cell reaction \( 2\text{H}^+ + 2e^- = \text{H}_2 \), and is expressed as the oxidation-reduction ('redox') energy level \( \text{H}^+/\text{H}_2 \). \((\Delta G \) is the Gibbs free energy of the reaction, \( n \) is the number of moles of electrons transferred, and \( F \) is the Faraday constant, 96490 coulombs/gram equivalent.) The dissociation potential of water is 1.23 eV, the difference between the \( \text{H}^+/\text{H}_2 \) redox level and the \( \text{OH}^-/\text{H}_2\text{O} \) redox levels in the liquid phase at 298 K. This difference is pH independent; the \( \text{OH}^-/\text{H}_2\text{O} \) level also shifts by \(-0.059 \text{ V/pH} \). Each redox couple is a density of electron energy states, with two distributions of states centered about the redox level. \(^{14}\) The redox level is a Fermi level; the distribution above the level is the unoccupied or oxidized state, and the distribution below is the occupied or reduced state. The splitting between the two states is caused by the Franck-Condon effect. \(^{15}\) The states themselves are electronic levels with rapid interstate
EvAC
EvAc
Ec
7
I/
_/.
H+/H2
OH-/H2O
0
Semi-Electrolyte conductor
pH 0
Helmholz layer
VH>O
Semi-Conductor
e
pH 14
Helmholz layer
VH<O
Electrolyte
XBL 8111-1546
Fig. 1-2
transitions compared to the slower vibrational and rotational transitions which cause the broadening of the distributions. The splitting is greater or smaller for weaker or stronger interaction between states. Thus in solution the distributions may be widely split, but may overlap significantly when the ions are adsorbed on a surface. See Figure 1-3.

Each redox couple may be considered to be like a semiconductor. At the junction between an electrolyte with a given redox couple and a semiconductor, charge may be transferred as in a semiconductor heterojunction, except that the charge transfer is accompanied by a molecular transformation. Electrons may move into the unoccupied reduced state, and holes into the occupied oxidized state. Also, such charge transfer may occur to or from either conduction or valence bands of the semiconductor, or surface states. The relevance of this is that both oxidative and reductive chemistry may occur on the same surface, separated by only an energy-level difference. Naturally such intimate chemistry would tend to suffer from back reaction. In the gas-phase experiment to be described, a spatial diffusion step helps to overcome this problem.

The probability of vertical electron state transfer at an interface is expressed as:

$$\nu = \int \nu(E) \, W_{\text{DONOR}}(E) \, W_{\text{ACCEPTOR}}(E) \, dE$$

where $W_{\text{DONOR}}(E)$ $W_{\text{ACCEPTOR}}(E)$ is the product of the density of states in the semiconductor and the density of states in the electrolyte, one being an acceptor, the other a donor. $\nu(E)$ is a transfer fre-
Franck condon splitting

Unoccupied—oxidized electron energy distribution

Occupied—reduced electron energy distribution

D.O.S.

Redox couple in solution

H^+ / H_2 couple absorbed on a surface. Note splitting is less, distributions may be unsymmetrical.

Fig. 1-3
quency factor. It is important to note that while redox levels do have an associated density of electron energy states, one must allow a reaction to have intermediate steps, and intermediate energy levels. Thus the chemical reactions written earlier give only the overall thermodynamic picture, and do not account for reaction pathway. Indirect processes involving energy dissipation may occur in addition to direct, or vertical transitions. These remarks are important, because it is by no means clear that the processes being described have overlapping densities of states. For example, it may be that one species of a redox couple adsorbs well on a surface, and the other poorly; this will ordinarily happen where one species is ionized and the other is not.

The previously mentioned reversibility of the platinum electrode with respect to the $\text{H}^+/\text{H}_2$ redox couple has the consequence that the Fermi level of the platinum will equilibrate with the Fermi level of this couple. Strictly speaking this only applies where the platinum is evolving hydrogen, or where there is molecular hydrogen present, so that the $\text{H}_2$ part of the couple is defined.

If other ions are present, they will also form redox couples. In an NaOH electrolyte, for example, the $\text{Na}^+/\text{Na}$ couple will exist, with redox level 2.7 V above the $\text{H}^+/\text{H}_2$ standard redox couple defined for pH 0. For reactions not involving the $\text{H}^+$ ion, the half cell potentials do not in principle change with pH. So in one molar NaOH this couple will be $2.7 + 0.059 \times 14 = 3.5$ V above the shifted $\text{H}^+/\text{H}_2$ couple. Since the $\text{Na}^+/\text{Na}$ couple is so far above the $\text{H}^+/\text{H}_2$ couple, and thus so far above the Fermi levels of the electrodes, it will
not participate in any charge transfer at the surface. Thus the net
effect of adding NaOH to water in our system is to increase the con-
ductivity of the electrolyte, to shift the \( \text{H}^+/\text{OH}^- \) ratio lower, and
that is all. For present purposes one need consider only the \( \text{H}^+/\text{H}_2 \)
and \( \text{OH}^-/\text{H}_2\text{O} \) couples, which will always exist in aqueous electrolytes.

C. Photoelectrochemistry

Using the description of electrochemistry just provided the photo-
electrochemical cell can be presented. Figure 1-4 shows the scheme
thought to describe such a cell, with a semiconductor electrode such
as n-type \( \text{SrTiO}_3 \). The vacuum level, conduction band, and valence
band of the semiconductor are shown bent upward near the interface
with the electrolyte. This is a Schottky-type barrier due to contact
potential difference with the electrolyte. The electrolyte is sup-
posed to have a greater density of charge carriers than the semicon-
ductor, and plays the role of the metal in a Schottky barrier. The
bending is upward because the Fermi level in the semiconductor has
fallen to the level of the Fermi energy in the cathode and electrolyte.

Before immersion in the electrolyte, the work function of \( \text{SrTiO}_3 \) is
above 4.2 eV. Assume the connection to the cathode is ohmic; this
can be assured by plating the platinum directly to the back face of
the semiconductor. The (electrochemical) work function of platinum
is 5.03 eV, larger than the work function of the semiconductor.

The contact potential difference will cause a flow of electrons from
the semiconductor into the platinum, the amount of flow depending
on the capacitance of the system and the initial contact potential
difference. There is some evidence that a Schottky barrier may form
Fig. 1-4
between \( \text{SrTiO}_3 \) and platinum,\(^{22}\) but electrical resistance measurements show no dependence on polarity, so the junction is assumed ohmic for the present purpose.

Band bending is critically important in photoelectrochemistry because electron-hole pairs created in the region where the bands are sloped will separate. This has the function of increasing carrier lifetime, and also of transporting them to regions where they are chemically useful. For bands curved upwards at the surface, holes will drift to the surface, and electrons will drift into the bulk and then into the cathode. A hole at the semiconductor-electrolyte interface may enter the occupied half of a redox couple in the electrolyte, as in the reaction: \( 2H^+ + 20H^- = H_2O + 1/2 O_2 \). The electrons are considered to enter the unoccupied half of the \( H^+/H_2 \) couple, which must be broad enough and close enough to the Fermi level that some unfilled states are at least within \( kT \) of the Fermi level of platinum.

Recall that an additional voltage bias was required in the original experiment of Fujishima and Honda. The reason was that electrons promoted to the conduction band of the semiconductor must flow into the platinum cathode, and then into the electrolyte at the \( H^+/H_2 \) redox level. For this to happen the bands in the semiconductor must be sloped in such a way that they are higher at the semiconductor-electrolyte interface than at the semiconductor-platinum interface. The amount of band bending will be given by \( V_{bb} = V_f - V_{fb} \) where \( V_{bb} \) is the voltage difference due to bent bands, \( V_f \) is the position of the Fermi level due to bias and contact potential difference, and
$V_{fb}$ is the position of the Fermi level when the bands are flat. See Figure 1-4. The flat band potential of TiO$_2$ is lower than the H$^+/H_2$ couple, so without bias, $V_{bb}$ will be negative when the Fermi level of the semiconductor equals the Fermi level of the H$^+/H_2$ couple.$^{23}$ The flat band potential of SrTiO$_3$ is higher than the H$^+/H_2$ couple, so that band bending will occur in the opposite sense.$^{24}$ Therefore an extra bias is needed for TiO$_2$ but not for SrTiO$_3$. See Figure 1-5. This is relevant because in the gas phase experiment there is no way of adding an external bias; if the system is analogous to the electrochemical system, it would make sense to use SrTiO$_3$ rather than TiO$_2$.

Any material used as an anode or cathode must have the property that it does not undergo irreversible corrosion. This makes highly oxidized oxides good candidates in aqueous electrolytes. It is believed that SrTiO$_3$ and TiO$_2$ are quite stable in aqueous cells.$^{25}$ A number of other materials, such as KTaO$_3$ and SnO$_2$, have also been used as anodes successfully. Also, other electrolytes, in which electrons are discharged to some other ion besides H$^+$ have been used.$^{29}$ However, the chemistry is thought to be similar in all these systems, so SrTiO$_3$ in aqueous electrolyte is a good model system.

I have used a simple contact potential difference model as a first approximation. In real systems one must consider the presence of intrinsic and adsorbate induced surface states, or equivalently, the possibility of chemical reactions. One may consider a hole at the surface of a semiconductor as equivalent to a broken bond in the material, a bonding state that is unfilled. The reaction with the OH$^-$ ion is the same as the attack of a chemical base. In SrTiO$_3$ there
Band energies $E^0$ for semiconductors before charge equilibration with electrolyte.

Fig. 1-5
may be a $\text{Ti}^{3+}$ state in the bandgap, for non-stoichiometric surface. In the presence of almost any adsorbate this ion is oxidized up to the $\text{Ti}^{4+}$ state, which is the state of Ti in stoichiometric $\text{SrTiO}_3$. This chemical picture may also be viewed as the transfer to an electron from a $\text{Ti}^{3+}$ level to an adsorbate level at or below it. It is not necessary to invoke surface states to explain the experiments to be described.

In the formation of the junction between $\text{SrTiO}_3$ and platinum, a transfer of electrons from the $\text{Ti}^{3+}$ level to the platinum is observed. This would be expected since the work function of platinum is so great. In any case, surface states will not exist on the adsorbate covered surface except momentarily when some species is desorbed from a site.

D. Photochemistry on Surfaces - Photocatalysis

I shall now discuss the relation of the electrochemical model to the gas phase experiments. The energy level considerations in electrochemistry give an indication as to whether a process will occur, but do not tell much about the kinetics of the process. The kinetics are controlled by catalytic properties of surfaces. In conventional catalysis one considers processes which run downhill thermodynamically. In electrocatalysis one considers processes at electrodes which involve charge transfer. The gas phase experiment is a kind of hybrid. It is a thermodynamically uphill process, and one which involves charge transfer but with no external circuit. It has a catalytic aspect in that the condition of the surface controls the kinetics of the reaction. But rarely is electrochemistry done at elevated temperatures and pressures, particularly photoelectrochemical research. The gas phase experiments are done at elevated temperatures and pressures
more typical of conventional catalytic reactions. Thus these experiments serve as a bridge between electrochemistry and catalysis.

Prior to this study, almost all photoelectrochemical research was done on liquid phase cells. The processes relied on ionic conductivity in the electrolyte; the conductivity of pure water would be insufficient. The prior work required the semiconductor to have high electrical conductivity in the bulk so that electrons could flow to the back face. Materials like TiO$_2$ and SrTiO$_3$ can easily be made conducting by reducing them in a hydrogen furnace or in vacuo at high temperatures. Oxygen leaves the crystal and it becomes n-type, typically with the Fermi level within a few tenths of an electron volt of the conduction band. As reduced oxides, they are subject to reoxidation in electrolytes, but the kinetics of this are slow, except for the surface layer. However, reduction does place the Fermi level higher in the gap than in the stoichiometric crystal. This may have the desirable effect of causing greater contact potential difference with the electrolyte, and hence more band bending.

If water were introduced onto the surface of a semiconductor from the gas phase it would be quite different from an aqueous electrolyte. Whereas liquid water has, at pH 7, $6 \times 10^{14}$ H$^+$ ions/cm$^3$, a monolayer or two of adsorbed water would contain essentially no H$^+$ ions if the ions were generated only by self-ionization as in the bulk. The adsorbed water would have no ionic conductivity; only surface diffusion could act to transport mass. The usual solvation effects on electronic energy levels would be missing. Solvation tends to raise energy levels towards the vacuum. This means that Franck-Condon
splitting of redox levels would be largely absent and electron energy
distributions would have occupied and unoccupied states overlapping
almost completely.\textsuperscript{30}

There are also similarities between the gas and liquid cases.
Most importantly, it is known that most oxide materials tend to adsorb
OH groups on their surfaces.\textsuperscript{31} This is referred to as hydroxylation.
As will be explained in the fourth chapter, these groups have important
effects on the surface properties. The other important similarity is
the bending of bands. Even if there are not ions to adsorb, the elec-
tron affinity of a layer of adsorbates will create a charged surface
and a space charge layer.

E. Electron-Hole Pair Generation and Separation

In both the electrochemical and gas phase experiments, the absorp-
tion of light by the semiconductor occurs by excitation of an electron
into the conduction band, leaving a hole in the valence band. Some
free carrier absorption occurs; excitation of conduction band electrons
in the reduced crystals is responsible for the dark color of \textit{SrTiO}_3
and \textit{TiO}_2.\textsuperscript{32} The intensity of light, and hence the number of pairs
created, falls off exponentially as \( I = I_o \exp(-za(h\nu)) \) where \( z \) is
the distance below the illuminated surface and \( a \) is the absorption
coefficient. In \textit{SrTiO}_3 the absorption coefficient increases roughly
exponentially from zero \( a \) the bandgap energy, 3.22 eV, to 8\times10^5 \text{ cm}^{-1}
at 4.8 eV.\textsuperscript{33} Thus one should consider that electron-hole pairs are
created in the region of a few thousand Angstrom units beneath the
surface. For the mercury lamps I used, 3200 Å is an average value.
SrTiO$_3$ is not strictly a direct gap material, but the direct transition is so strong that no phonon assisted light absorption is observed. Therefore absorption and recombination will be efficient, so that it is necessary to separate electrons and holes to lengthen their lifetimes. Recombination is a major source of inefficiency in electrochemical cells, increasing an external voltage bias between anode and cathode can bring the ratio of photons absorbed to bonds broken in water to unity. Of course, this external bias could be overcoming other 'overvoltages', but the larger internal electric fields act to separate charges more efficiently.

Charges can be separated by drift due to potential gradients, or by diffusion due to concentration gradients. Drift is clearly preferable for moving charges to a surface, especially for carriers of low mobility. Drift will be caused by sloping the conduction and valence bands so that electrons find positions of lower energy and holes find positions of higher energy. With no external potential, one can bend the bands by providing a junction at the surface through which the light enters. This can take the form of a change in doping near the surface, a layer of adsorbates on the surface, an intrinsic surface state, or a heterojunction with a material of different chemical potential. In an electrochemical cell, one has both a heterojunction with the electrolyte, and a layer of adsorbates, the Helmholtz layer, which affect band bending.

It is desirable for the characteristic depth of band bending to match the absorption depth for light, and for the band bending to be as strong as possible.
During illumination, charges are created in the region where the bands are bent; this tends to flatten the bands. It is for this reason that the Fermi level for flat bands, the flatband potential, must lie at or above the $\text{H}^+/\text{H}_2$ redox couple.

The characteristic depth for band bending is the bulk screening length or effective Debye length:\(^\text{36}\)

$$L_D = \left( \frac{\varepsilon kT}{4\pi e^2(n_b + p_b)} \right)^{1/2}$$

where $n_b (p_b)$ is the bulk value of the electron (hole) density and $\varepsilon$ is the static dielectric constant ($\varepsilon = 307$ for $\text{SrTiO}_3$) $L_D$ is a natural length encountered when solving Poisson's equation for the potential in the space charge region. This equation may be solved using different approximations depending on whether the semiconductor is intrinsic or extrinsic, and on how severe the band bending is. In this work only large bandgap materials are considered, and upward band bending creates only a depletion layer near the surface, not an inversion layer. For a large gap intrinsic material, the characteristic length is large; for $\text{SrTiO}_3$ at room temperature, $L_D = 2 \times 10^{-3}$ cm where I have used $n_b = 10^{12} \text{ cm}^{-3}$. This value of $n_b$ was inferred from $n_b = 1/(\rho \mu)$ (where $\rho$ is the resistivity and $\mu$ is the mobility) using a room temperature resistance measurement of crystals used in other experiments. For the reduced materials with $n_b = 10^{19} \text{ cm}^{-3}$, the characteristic length is 65 Å. This carrier density corresponds to a removal of about 0.1% of the oxygen atoms in the stoichiometric crystal.

Numerical solutions of Poisson's equation show a different curve shape between intrinsic and extrinsic materials. The extrinsic material has almost constant band slope beneath the surface, and the in-
trinsic material has sharply curved band bending, as shown in Figure 1-6. This effect causes the value of the potential to drop to one-half the value at the surface in 2-3 times less distance for intrinsic than extrinsic materials with the same $L_D$. This may affect my experiments because I used intrinsic materials.

SrTiO$_3$ has very low mobility; the electron mobility is 6 cm$^2$/volt-sec at 300 K, and falls within increasing temperature. The hole mobility is unmeasured, but is assumed low. An electron promoted to the conduction band 65 Å below the surface in a constant field of 1 V/65 Å requires $7 \times 10^{-14}$ sec to come to the surface. But an electron promoted to the conduction band 3200 Å below the surface in a constant field of 1 V/3200 Å requires $1.7 \times 10^{-10}$ sec. The first time corresponds to typical short free carrier lifetimes, the second time is much longer. Therefore an intrinsic material at room temperature with reasonable (IV) band bending would show little reactivity because so many carriers would be lost to recombination.

In most of the experiments to be described, as stoichiometric crystal with low conductivity was used. When a reduced crystal was used, no different effects were observed. In the high temperature water vapor environment of these experiments, the dark colored, reduced crystals became more transparent, indicating oxidation. I did not want to confuse hydrogen produced from oxidation of the semiconductor with that produced by photochemistry, so reduced crystals were not used. In the gas-phase experiment, conductivity through the bulk is not necessary; the active region is the surface only. There is the possibility that some band bending could be obtained by using
\( \phi \) for extrinsic material

\( \phi \) for intrinsic material

Distance into semiconductor

Surface

Potential

Fig. 1-6
a reduced crystal which was oxidized on the surface, as in Figure 1-7. This may be what is seen in UPS investigations of surface oxidation.

The reason that useful absorption occurs in the stoichiometric case is that the experiments were run at higher temperature than the room temperature electrochemical experiments. The ratio of the number of electrons in the conduction band due to thermal excitation at two temperatures is:

\[
\frac{n_1(T_1)}{n_2(T_2)} = \left(\frac{T_1}{T_2}\right)^{3/2} \exp \left[ -\frac{(E_c - E_F)}{kT_2} \left(\frac{T_2}{T_1} - 1\right) \right]
\]

where \(E_c\) is the energy of the conduction band and \(E_F\) is the Fermi energy. It is assumed here that the statistics are non-degenerate.

For intrinsic SrTiO\(_3\) with bandgap 3.22 eV, the ratio of electrons in the conduction band at 425 K to the number at 300 K is about 1.9 \(\times\) 10\(^8\), bringing the carrier concentration up to the range of the reduced material. At higher temperatures the bandgap becomes somewhat smaller; upon heating the clear stoichiometric crystal becomes yellow.

The discussion above centers on the effects of band bending, but not on what means are used to produce the effect. It was mentioned that a Schottky barrier model could be invoked for the case of a semiconductor-electrolyte junction. But in the gas-phase system, band bending must be caused by neutral adsorbates. Without reasonably strong band bending, no photochemical effects should occur. Strong band bending may be caused by a small fraction of a monolayer. 38

The Fermi level will tend to shift to the energy level of the adsorbed
Reduced bulk

Intrinsic surface layer

$E_C$

$E_F$

$E_V$

Fig. 1-7

XBL 8111-1541
species, and to stop shifting when this level is reached. If this occurs the Fermi level is said to be pinned. It has become independent of the bulk carrier concentration. The Fermi level is related to the adsorbate level by:

\[
\frac{[\text{OCCUPIED STATES}]}{[\text{UNOCCUPIED STATES}]} = \frac{[\text{REDUCED SPECIES}]}{[\text{UNOCCUPIED STATES}]} = e^{-\frac{(E_F - E_S)}{kT}}
\]

where \(E_s\) is the energy of the surface level and \([---]\) represents concentrations. \(^{39}\) Thus \(E_F\) will be pinned at:

\[
E_F = E_s + kT \ln \frac{[\text{OCCUPIED STATES}]}{[\text{UNOCCUPIED STATES}]}
\]

Figure 4 shows that one can think of the band edges at the surface remaining fixed, and bending in the space charge region to accomodate the shifted Fermi level in the bulk. The greater the initial energy difference between the Fermi level and the adsorbate level, the stronger the band bending. It is known that in the case of water adsorbed in SrTiO\(_3\), the water electron energy levels are below the top of the valence band. \(^{40}\) The Fermi level is probably not pinned in this system because the separation of the water levels and the Fermi level is too large. But it is reasonable to expect band bending on the order of one volt. Henrich, Dresselhaus, and Zieger report that for SrTiO\(_3\), the Fermi level falls by about 1 volt upon adsorption of water. \(^{41}\) If the band edges stay fixed at the surface, then this indicates one volt of band bending. Knotek reports a 1-2 volt shift in electron stimulated desorption spectra from SrTiO\(_3\), which corresponds to upward band bending by this amount. \(^{42}\) In the case of liquid water the effect is different because there are H\(^+\) and OH\(^-\) ions to be adsorbed, and their energy levels lie in the bandgap of SrTiO\(_3\).
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CHAPTER 2
WATER DISSOCIATION EXPERIMENTS

A. Introduction and Literature Survey

In this chapter I shall describe original experiments in which water is adsorbed and dissociated on the platinized surface of SrTiO₃ using ultraviolet light. There have been other attempts to observe dissociation of water adsorbed from the gas phase onto illuminated semiconductor surfaces. Schrauzer and Guth reported hydrogen and oxygen evolution from illuminated TiO₂ powder at room temperature under argon saturated with water vapor.¹ They obtained about $10^{16}$ molecules of hydrogen in two hours of irradiation of two grams of two micron powder in a batch reactor. Van Damme and Hall repeated this experiment in a flow reactor in order to remove the products so that equilibrium concentrations would not be reached.² They found no more hydrogen than Schrauzer and Guth, and observed that the reaction rate declined rapidly in time.

Sato and White observed hydrogen production from platinized TiO₂ powders.³ They obtained about $10^{17}$ molecules per hour from 0.25 g of powder which had an estimated area of 11 m²/g. They also reported hydrogen production in small amounts from TiO₂ powder without platinum. They concluded that oxygen vacancies on the reduced TiO₂ could account for the hydrogen production, even though the effect was photo-accelerated. Chung,⁴ Lo,⁵ and I observed small amounts of hydrogen production from water adsorbed onto powdered SrTiO₃ at room temperature, but these results could easily be explained by the reaction $xH_2O + C = CO_x + xH_2$, which is exoergic. Carbon is a universal con-
taminant, and was observed on these pressed powders with Auger electron spectroscopy.

Sakata and Kawai found that mixtures of \( \text{TiO}_2 \), \( \text{RuO}_2 \) and C would yield \( \text{CO} \) and \( \text{H}_2 \) under ultraviolet light. \(^6\) \( \text{RuO}_2 \) is used as an oxygen electrode. Sato and White also noticed \( \text{CO}_2 \) production in their experiments with platinized \( \text{TiO}_2 \), though there was no intentional source of C. These experiments failed to produce hydrogen if the \( \text{TiO}_2 \) were not reduced; again this argues for reduction of water by oxygen vacancies.

Because of these problems, I decided to use single crystal substrates. A monolayer or two of carbon or oxygen vacancies would not matter if hundreds of monolayers of hydrogen could be produced relative to the surface area of the crystal. In none of the powder experiments was more than a monolayer equivalent of hydrogen observed, so the experiments cannot be interpreted as photocatalytic. In single crystal experiments on \( \text{TiO}_2 \) I saw no hydrogen production, even on the platinized surface. Thus \( \text{TiO}_2 \) seems to suffer from the same disadvantage relative to \( \text{SrTiO}_3 \) in the gas phase experiment as in the aqueous electrochemical cell.

The diffusion of oxygen vacancies from the bulk to the surface could affect the interpretation of water dissociation data even on single crystal \( \text{SrTiO}_3 \). Walters and Grace studied the diffusion of oxygen vacancies and found a diffusion coefficient \( D = 3 \times 10^{-6} \text{ cm}^2/\text{sec} \) at 1200 K. \(^7\) Extrapolating to the temperature range of the gas phase experiments described in this work, \( D \) is still in the \( 10^{-6} \text{ cm}^2/\text{sec} \) range. Assuming a large defect gradient of \( 10^{20}/\text{cm} \), corresponding
to a heavily reduced sample, as many as $10^{14}$ vacancies/cm$^2$-sec could diffuse to the surface. This further complicates the powder results, because even if the defects on the surface were removed, the defects from the bulk could easily explain the results observed. In this work single crystals were used many times with no noticeable loss of activity. Reduced crystals showed no more activity than stoichiometric crystals, though they did appear to oxidize. Even if a $1\text{ mm} \times 1\text{ cm}^2$ crystal had $10^{19}$ vacancies/cm$^3$ this would explain only one experiment's yield, about $10^{18}$ molecules. Therefore I conclude that oxygen defects cannot account for the yields to be reported.

B. Mechanism and Electrochemical Model

In the first chapter I indicated that hydrogen evolution on platinum was considered to be a facile and somewhat understood process. In the gas phase experiment platinum apparently acts as a catalyst for hydrogen recombination. This means that hydrogen liberated from water on the semiconductor surface migrates to the platinized areas of the surface, combines into molecules, and desorbs. Platinum is an excellent catalyst for this step because it has a very low heat of adsorption for hydrogen, about 15-30 kcal/mol.\textsuperscript{8} Hydrogen desorbs from polycrystalline platinum at about 375 K.\textsuperscript{9} This is another reason to run above room temperature.

The picture for oxygen evolution from SrTiO$_3$ or other metal oxides is not as clear. Intermediates are likely to be involved. For a reduced SrTiO$_3$ crystal with one volt of band bending in the electrochemical cell, the valence band edge is about 0.8 volts below the OH$^-$/H$_2$O redox couple. The charge transfer formula \textsuperscript{11} would predict little
hole transfer to the occupied electron states of this couple unless the distribution were centered low enough, or were broad enough to overlap with the valence band. The shape and location of the energy states for $\text{H}^+ / \text{H}_2$ and $\text{OH}^- / \text{H}_2\text{O}$ have not been measured. No other redox couples are located near the valence band edge in this simple system. Surface states could be invoked to explain charge transfer; if a state were located at the position of the couple, holes could jump from valence band into the gap state, and then into the electrolyte. The $\text{Ti}^{3+}$ state has been investigated in this connection. It is located about 0.6 eV below the Fermi level, which is above the $\text{OH}^- / \text{H}_2\text{O}$ redox couple by 0.63 eV. It is about one volt wide. It is very strongly affected by water; adsorption of water depopulates the state completely. Even if $\text{Ti}^{3+}$ were correctly placed to exchange charge with the $\text{OH}^- / \text{H}_2\text{O}$ redox couple, it would have to be populated with electrons by the action of light in order for holes to jump into it. Chemically this means that $\text{Ti}^{4+}$ ions would take electrons from adsorbed water, become $\text{Ti}^{3+}$ ions, and then give the electron to the O(2p) derived valence band. There is evidence that light can restore $\text{Ti}^{3+}$ on a surface that has been exposed to water, but there is no evidence that this charge transfer scheme takes place cyclically during photocatalytic dissociation of water. The $\text{Ti}^{3+}$ may be limited to adsorbing a layer of $\text{OH}^-$ once, and further reactions may occur on the hydroxylated surface. Hydroxylation is discussed more fully in Chapter 4.

Sakata and Kawai have analyzed the energy levels of various species in aqueous solution at the semiconductor-electrolyte interface. This information is useful for comparison with the gas phase.
energy levels. Figure 2-1 shows the scheme they arrived at. They conclude that the highest occupied levels of 'OH and H₂O are lower than the OH⁻/H₂O redox couple, and lower than the valence band edge. But they claim that the OH⁻/H₂O occupied states do lie in a position that overlaps the slightly bent valence band of SrTiO₃. Therefore, oxidation of OH⁻ would be the most likely process in basic solution. For this reason, basic electrolytes would be preferred over acidic ones. At pH 0 there are only 6.02×10⁷ OH⁻ ions/cm³ in a solution. This may be compared with the 10¹⁴-10¹⁵ atomic sites per square centimeter on a semiconductor surface, or the 10¹²-10¹³ ions/cm² needed to pin the Fermi level.

These considerations led me to the concept that hydroxylation of the surface of SrTiO₃ is of great importance in the photodissociation of water. And hydroxylation is known to occur readily on most metal oxides merely in the presence of gas phase water.¹²

Sakata and Kawai conclude that the most likely surface reaction to evolve oxygen has a hydrogen peroxide intermediate.¹³ The steps are: h⁺ + OH⁻ = OH, OH + OH = O⁺ + H₂O, and O⁺ + O⁺ = O₂. Hydrogen peroxide has been observed during photoelectrochemical dissociation of water, and it has been found that materials like TiO₂ and SrTiO₃ are excellent catalysts for the decomposition of hydrogen peroxide. The reaction 2H₂O₂ = 2H₂O + O₂ is accelerated on the illuminated surfaces of these materials. Clechet, et al. observed H₂O₂ on the surface of TiO₂ in a photoelectrochemical cell by means of cyclic voltammetry.¹⁴ They managed to create even more H₂O₂ by platinizing the surface of the TiO₂. Wrighton noticed H₂O₂ in photoelectrolysis of water on
Fig. 2-1
SrTiO$_3$, but pointed out that since $\text{H}_2\text{O}_2$ is unstable in basic solutions, it is decomposed immediately upon formation.\textsuperscript{15}

In two of the steps of the above reaction path a geometrical effect would be noticeable. For the formation of $\text{H}_2\text{O}_2$ and for the formation of $\text{O}_2$, two sites with adsorbed OH or O, respectively, would need to be near each other, unless one postulates surface diffusion.

It has been observed in electron spin resonance studies that reduction of TiO$_2$ causes Ti$^{3+}$-Ti$^{3+}$ pairs to form at oxygen vacancies.\textsuperscript{16} These pairs could provide adjacent sites for the above processes. High temperature annealing removes these pairs in TiO$_2$, though apparently not in SrTiO$_3$.\textsuperscript{17} See Figure 4-1 for a view of the SrTiO$_3$ (001) crystal plane.

C. Experimental

The experimental apparatus used for these experiments was specially designed and built. Early in the experimental program an attempt was made to use a high pressure cell in a conventional ultrahigh vacuum chamber. This is a cell which may be closed over a crystal sample and exposed to pressures higher than one can allow in the vacuum system (above $10^{-5}$ torr) but which may be evacuated and opened to expose the crystal to ultrahigh vacuum surface characterization probes. This approach was unsuccessful here, though I returned to it in the fourth chapter.

The problem appeared to be that the vapor pressure of water at room temperature is at most 19 torr, and in order to get higher water vapor pressure it would be necessary to heat the cell. Since I selected gas chromatography over mass spectroscopy as a gas analytical technique,
a gas circulation loop was required between the cell and the gas chromatograph. It would have been very hard to heat the cell and a loop to uniformly high temperature in order to create a high vapor pressure of water. Since I saw virtually no water dissociation products at 20 torr, I thought that a higher pressure would be necessary, so a new apparatus was constructed. In retrospect, it may be that crystal temperature rather than vapor pressure was the important factor, but it is difficult to heat a crystal like SrTiO$_3$ without heating its environment. By putting the whole reaction chamber and vapor circulation loop in the oven of a gas chromatograph, I was able to obtain water vapor pressures as high as 15 atm, the vapor pressure of water at 472 K. The apparatus consisted of a circulation pump, the reaction cell, and a sampling valve, all constructed of stainless steel.

The sampling valve was a six port valve with a purged housing. The housing was filled with argon slightly above atmospheric pressure so that no other atmospheric gases could enter the valve and contaminate the experimental gases. The valve was fitted with a 0.25 cm$^3$ loop through which gases circulated except at sampling time. At that time the loop was switched so that its contents were forced by the carrier gas into the column of the chromatograph. The carrier gas was argon. The column for the water dissociation experiments was molecular sieve 5A. When the sampling valve was switched back to the normal position an amount of carrier gas equal to the loop volume at above 3 atm was admitted into the cell. This was assumed to have no effect on the experiment; the argon used contained no measurable
amounts of hydrogen or hydrocarbons. Sampling was done automatically at one hour intervals for about 20 hours usually. Since the volume of the cell was about 100 cm$^3$, twenty samples had no appreciable effect on the amount of gas present.

After being separated on the column, the sampled gases were detected by a thermal conductivity detector. The thermal conductivities of oxygen, argon, and hydrogen are in the ratio 58:39:419 at 273 K. This means that the detector is much less sensitive to oxygen than to hydrogen. The only other practical carrier would have been helium, which would give poor sensitivity to hydrogen. Therefore I monitored only the hydrogen. Evidence for oxygen production will be discussed later.

Because of the unreliability of mechanical circulation pumps run at high temperatures, it was necessary to construct a special pump to circulate gases through the sampling valve and reaction cell. I designed a thermal pump which would alternately evaporate and condense water. The circulation loop was broken and each end was terminated with a piece of stainless steel tubing which was fitted inside a heat sink. The two heat sinks were placed outside the oven, and wrapped with heating wires. A controller sent current through one heater for one minute, waited two minutes, sent current through the other heater for one minute, waited another two minutes, then repeated. During the time when one heater was on, water would evaporate from the enclosed tubing; all of the rest of the time the heat sink would cool the tube and allow water to condense. The pump controller was synchronized with the controller of the sampling valve so that samples
were taken at the same point in the heating cycle for all experiments. The water vapor was assumed to cause hydrogen created by photodissociation in the cell to circulate along with it. One hour intervals between samples allowed ten six minute circulation cycles; this was found to give adequate mixing. The system is illustrated schematically in Figure 2-2.

Ultraviolet light was provided by a 500 W high pressure mercury discharge lamp whose output was directed through quartz optics and a sapphire window in the side of the reaction chamber. The lamp emits strongly in resonance lines at 4.1, 3.94, 3.75, and 3.44 eV which are above the bandgap of SrTiO₃. With a calibrated Eppeley pyrheliometer I determined that about $6 \times 10^{16}$ photons/sec with energies above the bandgap fell on the crystal, which had roughly 1 cm² exposed to the light. Generally I used no infrared or visible filters so that about 90 mW of light power fell on the crystal. This may have raised the temperature slightly, but the effect would not be important in several atmospheres of water vapor.

A typical experiment was performed in this sequence: A crystal was prepared and placed in a sample holder so that one face was normal to the incident light. The cell was sealed using a copper gasket, and evacuated down to the ultimate pressure of a liquid nitrogen cooled sorption pump, about 10⁻³ torr. This means that for a crystal with 1 cm² area there is about one monolayer of air left in the cell. A metal sealed valve immediately attached to the cell was then closed, and reactants such as water were introduced by injection from a syringe through a chromatography septum. The water used had a resistivity of
Six minute timer

One hour timer

Motor

SrTiO_3 single crystal with platinum on side facing light

UV light

Sapphire window

Reaction cell

Loop

Sampling valve

Constant temperature oven of gas chromatograph

To sorption pump for initial evacuation

Reversing valve motor controller

Thermal pump

Argon in

Six minute timer

Reversing valve motor controller

Fig. 2-2
at least $10^7$ ohm-cm and was boiled before injection to drive out any dissolved gases.

In most experiments the crystal was coated on one side with metal, usually platinum. This side would then be the one facing the light. The platinum was evaporated from a tungsten filament in a sorption and ion-pumped bell jar, with background pressure in the $10^{-6}$ torr range. In the first several months of experiments no control over platinum evaporation was attempted. In an effort to obtain more reproducible results, a photocell was placed under the translucent crystals of SrTiO$_3$ and light from the evaporation filament was monitored. As the crystal darkened due to platinum coverage, the resistance of the photocell increased. The crystal was rough polished before each experiment. This left a matte surface which would not be covered by metal evaporated from one small source. The amount of platinum was such that a visible darkening of the crystal occurred. The amount of platinum on the surface caused about 15% less light to pass through the crystal.

The crystals of SrTiO$_3$ which I used were of nominal (111) orientation, but because they were roughly polished, they probably had a high portion of the (001) cleavage planes exposed. They had an area of 1-2 cm$^2$ so that a figure of $10^{15}$ molecules was taken to be one monolayer. The amount of hydrogen detected by the gas chromatograph was calibrated by filling the cell with a known pressure of hydrogen and sampling normally. This calibration was run periodically and was found to give consistent results.
D. Results

Figure 2-3 shows hydrogen peak height versus time for typical experiments. Since the system is a batch reactor, this is a record of total hydrogen accumulation. In these experiments platinum was deposited on stoichiometric SrTiO$_3$ crystals, and water vapor was allowed to fill the cell to its saturation vapor pressure. The main point of interest is that amounts of hydrogen were created which were far in excess of those which one would expect from stoichiometric reactions of the type mentioned in connection with powder experiments. The reaction is therefore catalytic; the surface activity of SrTiO$_3$ is regenerated several hundreds of times. These curves generally showed three stages: an induction period of 1-2 hours, a period of growth, and a leveling off after about 10 hours.

The induction period seems to be unrelated to light exposure. A crystal can be exposed to water vapor at typical experimental temperatures and pressures in the dark and no hydrogen production will be observed. If the light is then turned on, after several hours in the dark, hydrogen production will begin immediately. But if a crystal is exposed to light in vacuo at the same temperature, the induction period is still observed after water vapor is introduced. Figure 2-4 shows the results of such experiments done at 425 K and the saturation vapor pressure of water, about 4.7 atm. Since hydroxylation of the crystal occurs very rapidly, the induction period is probably related to a slow cleanup reaction, such as the removal of carbon from the platinum. A shorter induction period is observed in the aqueous photo-electrochemical cell. 19
\( H_2 \) production (\( 10^{15} \) molecules)

Fig. 2-3

\( \sim 32 \) monolayers
Water in Light on Light on Water in Time (hours)

Fig. 2-4
During the period of strong hydrogen production, recombination of oxygen and hydrogen can occur both on platinum and on SrTiO$_3$. If this back reaction were inhibited by removing the oxygen, one would expect the equilibrium to be shifted so that more hydrogen would be observed. By introducing 1-2 g of 1 mil copper ribbon into the cell I found that about twice the former amount of hydrogen would be observed. By introducing 1-2 of 1 mil copper ribbon into the cell I found that about twice the former amount of hydrogen would be observed. See Fig. 2-5. I also found that if the copper gasket used to seal the cell were heavily pre-oxidized, less hydrogen would be observed. Blank experiments showed that the reaction Cu + H$_2$O = H$_2$ + CuO did not occur to a measurable extent. Also it was found that if oxygen were introduced into the cell with the copper, the amount of oxygen would decrease. These experiments indicate that oxygen is produced in the decomposition of water, and that it participates in the back reaction.

The levelling off of the amount of hydrogen observed is due not only to equilibrium between forward and back reactions. There is also some type of poisoning that occurs. If an experiment on a crystal is repeated after pumping the gases from one experiment away and replacing the water, less hydrogen is produced. Normally an experiment was preceded by repolishing a crystal and recoating it with platinum. Poisoning was also observed in the aqueous electrolyte cell, and it was found that replacing the platinum cathode would restore the activity. 17

Hydrogen production curves from one experiment to the next were repeatable to only about 30%. Also, there were two classes of curve shapes, as shown in figure 2-6. The curves of type I can be modelled
Fig. 2-5
Hydrogen accumulation

\[ H = H_0 (1 - \exp \left(\frac{T}{T_0}\right)) \]

- ○ Experimental Type I
- △ Experimental Type II

Time (hours)
by a simple exponential law of the form \( H = H_0 (1 - \exp(t/t_0)) \) where \( H \) is the amount of hydrogen observed, and \( t \) is the time starting at the end of the induction period. This is the type of relation one would expect from a forward-back reaction equilibrium. However, curves of type II would be characteristic of a poisoning mechanism which affects the early stages of the reaction. Poisoning could occur in curves of type I, but probably earlier or later. The two types of curves occurred in approximately equal numbers, and there was no apparent correlation with experimental conditions.

One possible poisoning mechanism that was investigated was the effect of CO on platinum. In a stainless steel cell of the type I used, a certain amount of CO is continuously emitted by the walls and is very likely to be displaced from the walls by chemisorbed water. CO is known to block surface sites on platinum and thus prevent the chemisorption of hydrogen. In these experiments platinum is placed on the semiconductor surface to act as a recombination catalyst for atomic hydrogen created in the photocatalytic dissociation of water on SrTiO₃. Intentionally introducing CO into the cell during an experiment should have the effect of inhibiting the rate of hydrogen production, according to this model. Figure 2-7 shows the results of an experiment where 1 torr of CO was added to 2 atm of water vapor at 395 K. Much less hydrogen is observed than without the CO. One might expect the water gas shift reaction \( \text{H}_2\text{O} + \text{CO} = \text{CO}_2 + \text{H}_2 \) to occur and actually increase the amount of hydrogen. Blank experiments showed that the system was not catalytically active enough at these temperatures to promote this reaction at appreciable rates. Studies described
Without CO

With 1 Torr CO

Fig. 2-7
in Chapter 4 show that CO is oxidized to CO$_2$ very readily on the surface of SrTiO$_3$ under these conditions. Thus CO might act like copper in removing extra oxygen so that more hydrogen would be seen. However, the overall effect of CO in these experiments was to poison the reaction. This further supports the model that platinum is active in hydrogen recombination.

A possible solution for the CO contamination problem is simply to raise the temperature above about 170°C, where CO would tend not to stick as well to platinum. Another possible solution is to use another metal in place of platinum and allow reactions like CO + 3H$_2$ = CH$_4$ + H$_2$O to take place. This subject is explored in chapter three. There may be other contamination problems in addition to CO.

Further insight into the mechanism of the reaction comes from the effect of different amounts of platinum coverage. Figure 2-8 shows hydrogen production at 120°C and 2 atm water vapor pressure for different platinum coverages. If no platinum is used the amount of hydrogen observed is no more than the background amount. If only a small spot of platinum is evaporated onto the middle of the crystal, somewhat more hydrogen is seen. Attempting to cover the crystal with a thick layer of platinum by evaporating it from several different angles results in small production. A grid of 0.5 mm spots of platinum, covering about half the surface area of the crystal gave better results, but a thin layer of platinum covering the whole face gave the best results. Electron micrographs of the rough polished surface revealed that such an evaporation would leave a great deal of unplatinized SrTiO$_3$ because of shadowing effects. In the case of the grid of plati-
Fig. 2-8

H₂ production (10^{15} molecules)

- Full, thin coating
- Grid covering, \( \sim 50\% \) Pt coverage
- Very thick coating
- Small spot only, \( \sim 5\% \) Pt coverage

\( \approx 32 \) monolayers
num, scanning Auger analysis showed that the islands of platinum did have sharp edges, with no detectable platinum in the masked regions. The conclusions to be drawn are that the reaction requires platinum, and that platinum put on in such a way as to give the shortest diffusion path for hydrogen created on the SrTiO$_3$ causes the most hydrogen to be created. An interesting variation was an experiment in which the platinum was applied in the form of a smoke. If about 5 torr of argon is allowed into the bell jar during evaporation, platinum atoms will collide, agglomerate, and precipitate onto the SrTiO$_3$ as particles. Putting the platinum on the SrTiO$_3$ this way resulted in reasonable rates of hydrogen production, even though the platinum-semiconductor interface was less intimate than with the conventional evaporation.

Blank experiments showed that if platinum is evaporated onto Al$_2$O$_3$ instead of SrTiO$_3$, no hydrogen is produced. Also, if the ultraviolet light above the bandgap of SrTiO$_3$ is blocked with a filter, no hydrogen is produced. Rhodium substituted for platinum worked in its place, but not quite as well. In electrochemical cells, rhodium has almost as low an overpotential for hydrogen as platinum. 21

A large number of experiments were performed to establish the dependence of hydrogen production rate to interpret because of poor repeatability. One expects the back reaction rate to increase exponentially with temperature according to a simple Arrhenius relation. The forward reaction rate would increase exponentially with temperature if it were conductivity limited. The poisoning rate is unknown, but
the curves of type II as in Figure 2-6 indicate that poisoning often occurs in the first three hours.

The hydrogen production rate depends rather weakly on illumination intensity; if only 15% of normal intensity is used, about 50% of normal hydrogen production is observed. This indicates that production of electron-hole pairs is not rate limiting. Also, if the high energy mercury spectral lines are filtered out, little reduction of hydrogen production is observed. The high energy lines, at 3.9 and 4.1 eV cause pairs to be created much more closely to the surface than the low energy lines, around 3.4 and 3.7 eV. This indicates that band bending is not rate limiting. Experiments were done to show that band-gap radiation was necessary to produce hydrogen; it was found that no hydrogen was produced if light above the band-gap was filtered out.

Several conclusions can be drawn from the exploratory experiments which have been described in this chapter. The dissociation of water adsorbed from the gas phase onto SrTiO₃ is catalytic in the sense that the surface is regenerated by light enough that several thousands of monolayers of products can be observed. The energy of the light must be above the band gap of SrTiO₃, but the creation of electron-hole pairs is not rate limiting. One can conclude that platinum is active in hydrogen chemistry, and that platinum or rhodium or some catalyst is essential for the reaction to proceed at reasonable rates. Also it is important that the platinum be distributed in small islands over the surface of the semiconductor. This may minimize the diffusion path of hydrogen from dissociation sites on SrTiO₃, or it may be a platinum-SrTiO₃ boundary effect. In any case, these results are much better
than those of the powder experiments, and cannot be interpreted as mere impurity effects.

There appear to be at least three chemically important reactions which occur. One is the forward dissociation reaction, one is the recombination back reaction, and one is the poisoning of the surface. Poisoning may affect the platinum or the SrTiO$_3$, or both, but the CO experiments suggest that poisoning of platinum could easily occur. Many of the problems encountered in this experiment are due to the use of a batch reactor. However, if a flow reactor were to be used, problems with detection sensitivity would arise. In any case, the role of carbonaceous species on the surface seems important; it will be discussed in Chapter 4.
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CHAPTER 3
SYNTHESIS EXPERIMENTS

A. Introduction and Literature Survey

In this chapter I will report the results of a number of experiments intended to show that methane can be synthesized from photochemically produced hydrogen. In the second chapter I showed that hydrogen could be obtained from dissociation of water in a photochemical reactor operating in the 375-475 K temperature range at several atmospheres of water vapor pressure. Hydrogen is a valuable product, which could be extracted from the cell and used in molecular form for further synthetic reactions. Many syntheses of hydrocarbons and oxygenated hydrocarbons are exoergic with H₂ and CO₂ as feedstocks, because of the large amount of energy in the molecular hydrogen bond. But there might be advantages to using hydrogen in the form of a surface atomic species, thus retaining the activation energy necessary for dissociation of molecular hydrogen. Surface OH species could also be used to synthesize oxygenated products like alcohols, formic acid, formaldehyde or acetaldehyde.

Another class of reactions that has been attempted is the synthesis of ammonia from photogenerated hydrogen and molecular nitrogen over a catalyst like iron. These syntheses might be a more valuable use of solar energy than simple production of hydrogen for use as a fuel. Both ammonia synthesis and methane synthesis are typically run in the 525 K temperature range, or above. This is well above the temperature range of conventional aqueous electrochemistry, and thus provides another reason to examine reactions at the gas-semiconductor
interface. Table 3-1 shows a number of synthetic reactions and their free energies. Only certain one-electron transfer steps of these reactions are likely to be driven by light.

One class of combined dissociation-synthesis reactions consists of those where molecular hydrogen is formed on a catalyst like platinum, as in the experiments described in Chapter 2. The hydrogen would then desorb, and readSORbe on a synthesis catalyst where it would react with a second species, such as CO CO₂ or N₂. The main advantage of this technique would be to protect hydrogen from back reactions. A more desirable class of reactions are ones where the platinum is replaced by a synthesis catalyst, so that atomic hydrogen would diffuse from the semiconductor directly to the surface where the second species was adsorbed. A further refinement would be to use a synthesis catalyst, such as Fe₃O₄, which also acted as a light absorber and water dissociator. However, a single material cannot be expected to act as the optimum substrate for two reactions at a given temperature and pressure.

Another type of reaction is one where light energy is transferred not only to water, but instead or in addition, to other molecules. A good example would be the dissociation of N₂ on a semiconductor in the ammonia synthesis reaction. This step is rate limiting on conventional iron catalysts, but the highly energetic sites represented by holes or electrons at semiconductor surfaces should promote facile adsorption. The advantage of transferring energy to other molecules besides water is that better matches between adsorbate electron energy levels and the bands in the semiconductor might be achieved.
TABLE 3-1

\[ \text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \quad \Delta G^\circ = -33.4 \text{ kcal/mol} \]

\[ 4\text{CO} + 2\text{H}_2\text{O} = \text{CH}_4 + 3\text{CO}_2 \quad \Delta G^\circ = -54.1 \text{ kcal/mol} \]

\[ \text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta G^\circ = -26.2 \text{ kcal/mol} \]

\[ \text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2 \quad \Delta G^\circ = +19.1 \text{ kcal/mol} \]

\[ 3\text{H}_2 + \text{N}_2 = 2\text{NH}_3 \quad \Delta G^\circ = -3.9 \text{ kcal/mol} \]

\[ 2\text{C} + 2\text{H}_2\text{O} = \text{CH}_4 + \text{CO}_2 \quad \Delta G^\circ = +2.87 \text{ kcal/mol} \]

\[ \text{C} + 2\text{H}_2 = \text{CH}_4 \quad \Delta G^\circ = -12.15 \text{ kcal/mol} \]
TiO$_2$, SrTiO$_3$ and other metal oxides have been used as photocatalysts in a number of reactions. Krautler and Bard photocatalyzed the Kolbe decomposition of acetic acid to CO$_2$, C$_2$H$_2$, and CH$_4$ by using a platinized TiO$_2$ powder and ultraviolet light.\(^1\) Djeghri et. al. observed the photooxidation of various alkanes to ketones and aldehydes on TiO$_2$.\(^2\) Great selectivity was achieved in many cases. A NASA group found that many organic compounds, especially formic acid, could be photosynthesized from CO and water on various oxides thought to be similar to soils on other planets.\(^3\)

Boonstra and Mutsaers reported the photo-hydrogenation of ethylene and acetylene on TiO$_2$.\(^4\) They noted that removing the OH groups from the TiO$_2$ by heating reduced efficiency and changed the product distribution. Saturated alkanes were found to be produced on the OH rich surfaces while unsaturated products came off the dehydrated surfaces. In no case were oxygenated products observed.

Most of the experiments mentioned in the last paragraph were performed with gas phase reactants at room temperature. There are others performed in liquid cells. Sakata and Kawai decomposed ethanol and water into hydrogen, methane, and acetaldehyde on TiO$_2$ coated with metals such as platinum, palladium, rhodium and nickel.\(^5\)

The reactions just described are generally exothermic with the light serving to activate the surface of the TiO$_2$, but not adding energy to the products. But Halman managed to add light energy in the reduction of carbon dioxide to formic acid, formaldehyde, and methanol on p-type gallium arsenide and gallium phosphide in aqueous solution.\(^6\)
Hemminger, Lo, Somorjai and I reported that a single crystal of SrTiO$_3$ in mechanical contact with platinum foil would synthesize methane from CO$_2$ and water vapor.\textsuperscript{7,8} We observed that about ten monolayers of methane would be produced at room temperature upon illuminating the reduced crystal with ultraviolet light in an atmosphere of 17 torr of water and 15 torr of CO$_2$. After producing ten monolayers of methane, the reaction stopped, well short of an equilibrium concentration of methane. It is a little surprising that we saw any methane, considering that platinum is a very poor methane synthesis catalyst. Van Damme and Hall noted the rapid poisoning of this reaction, and pointed out that it could be explained in terms of a stoichiometric reaction, rather than a catalytic reaction.\textsuperscript{9} At least it was done on a single crystal. Most of the work just cited on TiO$_2$ was on powder surfaces, with the attendant contamination problems mentioned in Chapter 2. An obvious improvement on our technique would be to raise the temperature to a conventional methane synthesis temperature, and to use a good methanation catalyst, such as rhodium, iron Fe$_3$O$_4$, or one of these with a promoter such as potassium.

B. Thermodynamics

In the experiments described in this chapter I attempted to synthesize methane from CO$_2$ and the H$_2$ derived from photodissociation of water. This is the Sabatier reaction: $4\text{H}_2 + \text{CO}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$. ($\Delta G = -22.78 \text{ kcal/mol at 400K and 1 atmosphere}$). This is not the only possible reaction with these reactants, however. Actually one must consider $\text{H}_2 + \text{CO}_2 = \text{C} + \text{CO} + \text{CH}_4 + \text{H}_2\text{O} + \text{O}_2 + \ldots$. Cairns and Tevebaugh have developed a sophisticated ternary phase diagram for
the C, H, O system which can be used to analyze the thermodynamics of the reaction. They find that only the species listed above, except O₂, will be present in significant amounts in equilibrium. The formation of CO is no problem, since it is even more useful in methane synthesis than CO₂. But there are two other problems. One is that elemental carbon may be formed. The second problem is the presence of water. If a lot of water is present as a source of hydrogen in the photo-dissociation step, it will also be present to drive the Sabatier reaction in reverse. The reverse of the Sabatier reaction is steam reforming. At low temperatures (600 K), steam reforming produces CO₂ and H₂ from methane and water. At high temperatures (above 1200 K) thermodynamics favors CO instead of CO₂. Assuming only the Sabatier reaction, one can calculate the equilibrium concentrations of methane. Suppose that the reaction runs at 400 K, that 1 atm of CO₂ and 1 atm of H₂O are present, and that a typical amount of hydrogen is present from photodissociation of water, about 1000 monolayers or about 4*10⁻⁴ atm. Then \( K_p = 3.1*10^{12} \approx \frac{P_{CH_4}}{P_{H_2}} \) and the equilibrium value of \( P_{CH_4} = 0.82*10^{-4} \) atm, which is 82% of the amount of CH₄ one would obtain if the reaction were to run to completion.

The problem with this reaction is that any catalyst which promotes the formation of methane will also tend to promote the reverse reaction. In the case of simple water dissociation, I was able to shift the equilibrium amounts of hydrogen created by removing the unwanted oxygen byproduct. But in this case, the unwanted byproduct is water, which is present in huge amounts to act as a source of hydrogen. Therefore,
the attempt to couple water dissociation with the Sabatier reaction runs into thermodynamic equilibrium problems. Still, it is interesting to see if catalytic production of methane occurs at all.

An important experiment was to see if the presence of a high pressure of CO₂ would affect the photodissociation of water on SrTiO₃. As will be shown in Chapter 4, CO₂ does adsorb on the surface of SrTiO₃ in the presence of water. I found at 425 K and with one atmosphere of CO₂ in the reaction chamber, that hydrogen production from water using ultraviolet light on SrTiO₃+platinum was not inhibited by the CO₂. In experiments like those in Chapter 2 except for the CO₂, amounts of hydrogen comparable to those produced without CO₂ were created. This was true for experiments run with and without copper ribbon in the cell to adsorb extra oxygen, and for experiments run at and below the saturation vapor pressure of water at 425 K. Blank experiments showed that no hydrogen was produced in the absence of ultraviolet light. Therefore it seems that CO₂ does not interfere with water dissociation.

C. Experimental

The apparatus used for the experiments in the rest of this chapter was essentially the same as that described in Chapter 2. The column of the gas chromatograph was changed to one packed with Chromosorb 102, and the detector was changed to a flame ionization detector. This allowed separation and detection of light hydrocarbons and alcohols, etc. Since the flame was air/hydrogen and since a flame ionization detector is insensitive to hydrogen anyway, hydrogen could not be detected. One of the first experiments was to establish the hydro-
carbon background and the contamination of reactants used. The CO₂ had a very slight amount of CH₄ in it, but this amount was not comparable to amounts which could be produced in reactions. CO₂ and other gases were injected into the cell through the septum, just like the water. The flame ionization detector is much more sensitive to methane than a thermal conductivity detector is to hydrogen. The detection limit was about one monolayer.

Experiments were run as in the water dissociation section. Samples were taken automatically at one hour intervals for about 20 hours. Crystals were freshly prepared before each run.

D. Results and Discussion

In this section I will present some of the results of about 50 experiments in methane synthesis. I attempted these experiments both with methane synthesis catalysts evaporated directly on the SrTiO₃, and with separate catalyst surfaces. Methane synthesis catalysts are transition metals such as nickel, iron, cobalt, rhodium, and ruthenium. In an atmosphere of water, most of these metals except Rhodium would oxidize severely, but oxides like Fe₃O₄ are also good methanation catalysts. I attempted methanation with rhodium, iron, ruthenium, and Fe₃O₄.

With transition metals evaporated directly on the SrTiO₃, one might expect the following reaction sequence: Hydrogen created from dissociation of water would diffuse to transition metal islands on the surface. Carbon dioxide would dissociatively chemisorb on the metal, and yield surface species like carbon monoxide or some activated (non-polymerized) form of carbon. Then hydrocarbon synthesis
would proceed as in Fischer-Tropsch synthesis. Methane would typically be the most abundant product, with smaller amounts of $C_2$ and higher C-number species. For the case of physically separate synthesis catalysts, the same sequence would apply except that hydrogen would desorb in molecular form from the semiconductor and readsorb and dissociate on the methanation catalyst. In both cases the water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta G = -5.86 \text{ kcal/mol @ 400 K})$$

would probably go on simultaneously.

At 450 K several experiments were run with about two atmospheres each of water and carbon dioxide. SrTiO$_3$ with platinum evaporated on it, as in the simple water dissociation experiments, produced no methane. But evaporated iron in patches on the platinized SrTiO$_3$ produced small amounts of methane. Most of the experiments which produced small amounts of methane produced roughly the same amount which was about 200 monolayers, or about $2 \times 10^{17}$ molecules of methane. Equilibrium was reached within 5-10 hours. It was this observation that led to the notion that there was a facile back reaction and that the ultimate amount of methane was limited by equilibrium.

If a rhodium foil were placed in the cell, but not in contact with the platinized SrTiO$_3$, it could be heated resistively without heating the crystal. Molecular hydrogen could adsorb on it after desorbing from the crystal where it was produced. Only the same small amount of methane as above was produced. The rhodium was heated in the range from 525-600 K while the cell was at 425 K. In some cases another chromatographic peak appeared which was found to have the same retention time as ethane; this is evidence of further Fischer-
Tropsch synthesis. If the rhodium foil were not heated, about the same amount of methane was seen. If an iron foil were substituted for the rhodium and heated in the same temperature range, about 700 monolayers of methane were observed on the first trial. However, I had observed in earlier experiments with water dissociation that iron oxidized in the presence of water to yield hydrogen under the conditions of those experiments. So this experiment probably gave the greater amount of methane because more hydrogen was present than would be from dissociation of water on platinized SrTiO₃. The effect of light was slight, and injecting additional hydrogen into the cell did produce much more methane.

Therefore I switched to completely oxidized iron. An iron foil 1 mil thick was thoroughly oxidized to black Fe₃O₄ in air and placed in the cell, but not in contact with the SrTiO₃. Only the usual small amount of methane was observed in an experiment with the whole system at 425 K. A quartz-halogen lamp was then placed in the cell in order to heat the Fe₃O₄. The lamp by itself produced no methane in a blank experiment at 425 K with two atmospheres of CO₂ and the saturation vapor pressure of water. With platinized SrTiO₃ in the cell, and with the lamp on so that the Fe₃O₄ was heated to about 525 K, the usual amount of methane was produced. Apparently, any of the catalysts which would promote methane synthesis would promote the reverse reaction. In most of these reactions there was a rapid growth to equilibrium, usually within the first few hours. After several experiments the small amounts of the Fe₃O₄ foils appeared to have turned slightly from black (Fe₃O₄) to red, indicating oxidation up to Fe₂O₃.
red areas were places where light from the mercury lamp struck the foil, which suggests that the oxidation was photoaccelerated. This may again have created excess hydrogen.

In a final set of experiments, rhodium and ruthenium were evaporated directly on the surface of SrTiO₃ without any platinum. The usual small amount of methane was observed for rhodium, but not as much as was observed in the case of ruthenium. Ruthenium oxidizes quite easily in these conditions, but rhodium should not; this might explain the difference between their performance.

The conclusions that may be drawn from these experiments are that methane is rather easily produced under the conditions established, but that back reactions limit the amount that may be observed to the equilibrium value. The dissociation of methane produces hydrogen, which in turn affects the hydrogen equilibrium, especially if platinum is present. Probably, the reasonable way to produce hydrogenated products is to separate the photodissociation process from the hydrogen production process. This remark will apply all the more to the case of ammonia synthesis, because of the much poorer stability of ammonia relative to methane.
REFERENCES


CHAPTER 4
ULTRAHIGH VACUUM EXPERIMENTS

A. Introduction and Literature Survey

The main object of the studies described in this chapter was to gain insight into the molecular details of reactions described in the previous two chapters. Ultimately one wishes to know the exact mechanism of the reactions, including all intermediate steps and their rates. These details are not all known, but new information is presented here, as well as a demonstration of the usefulness of ultrahigh vacuum analytical techniques.

These studies are mainly concerned with the interaction between the surface of SrTiO$_3$ and adsorbates on it. Since the principal adsorbate was water, the chemisorbed species most of interest are H, OH, H$_2$O, and O. I had no good way to detect hydrogen except thermal desorption, and oxygen is part of the bulk of the crystal, so the most convenient species to monitor is OH. Also, for reasons to be presented, surface OH appears to have a prominent role in photochemistry.

In the following discussion I will refer to SrTiO$_3$ in relation to TiO$_2$, upon which relatively more research has been conducted. SrTiO$_3$ has a cubic perovskite structure with titanium ions octahedrally coordinated to titanium in all three. Electronically, both SrTiO$_3$ and TiO$_2$ have Ti (3d) derived conduction bands, and O (2p) derived valence bands. The electronic energy levels of strontium in bulk SrTiO$_3$ are about 15 eV above and below the top of the valence band, so they should not ordinarily be chemically active.\(^1\) Also, the cleavage plane of SrTiO$_3$, the (001) plane can show two different compositions, one with
titanium cations (type I) and one with strontium cations (type II). Since the electronic energy levels of strontium are unavailable, the chemically active surface should be of type I. In an ionic solid like SrTiO$_3$, one expects holes and electrons at the surface to be rather localized. Thus electrons and holes should cause chemical activity in the titanium derived conduction band or the oxygen derived valence band or the Ti$^{3+}$ surface state, but not in strontium.

Some strontium related effects have been noticed. Bermudez and Ritz claimed that a peak at 6.8 eV in the electron energy loss spectrum of SrTiO$_3$ is associated with the strontium ion, and is affected by oxygen exposure. Knotek has reported a high density of Sr-H species, (but very little Sr-OH) on SrTiO$_3$ using a technique called electron-excited Auger stimulated desorption. There is no evidence that strontium related species participate in photochemistry on the surface.

In SrTiO$_3$ and TiO$_2$, the titanium ion is Ti$^{4+}$ and the oxygen ion is O$^{2-}$. The strontium ion in SrTiO$_3$ is Sr$^{2+}$. Upon reduction in vacuum or in a hydrogen atmosphere at elevated temperatures, oxygen vacancies are created in both crystals. Removing an oxygen atom causes two electrons to be left in the crystal, allowing two Ti$^{4+}$ ions to go to the Ti$^{3+}$ state. Titanium interstitials can also be created by reduction. From electron spin resonance studies, the existence of Ti$^{3+}$ ions in reduced TiO$_2$ has been confirmed. It is also possible to create Ti$^{3+}$ ions at the surface by ion bombardment in vacuum. A beam of Ar$^+$ ions will preferentially remove oxygen atoms (mass 16 amu) which are lighter than titanium (mass 50 amu) or strontium (mass 88 amu).
Note that removing an $O_2^-$ ion connects a $\text{Ti}^{3+} - \text{Ti}^{3+}$ pair.

Fig. 4-1
The existence of Ti$^{3+}$ on the bombarded surface of TiO$_2$ and SrTiO$_3$ has been inferred from XPS and ELS measurements.\textsuperscript{6,7} The Ti$^{3+}$ ion on the surface is very strongly affected by adsorbates. Upon adsorption of oxygen, hydrogen, or water, the Ti$^{3+}$ signal is strongly suppressed. Apparently any of these species can act as an electron donor to Ti$^{3+}$. Knotek has reported Ti-H, Ti-O, and Ti-OH on the surface of SrTiO$_3$.\textsuperscript{8} Some authors have postulated that oxygen photodesorption in photocatalytic processes results in the creation of Ti$^{3+}$ sites on the surface, which in turn act as sites for further chemisorption of water.\textsuperscript{9} However, water does adsorb on surfaces of TiO$_2$ and SrTiO$_3$ which are poor in Ti$^{3+}$, though not as well. Adsorption of water removes the Ti$^{3+}$ states on SrTiO$_3$, but does not affect Ti$^{3+}$ on TiO$_2$.\textsuperscript{10} But, annealing at high temperatures, above 1000 K, will remove the Ti$^{3+}$ on TiO$_2$, but no on SrTiO$_3$.\textsuperscript{10} Ti$^{3+}$ is evidently destroyed by oxygen diffusion from the bulk. Apparently both electronic and geometric affects play a role in chemisorption on these surfaces.

Boehm argues that H$_2$O will tend to hydroxylate metal oxide surfaces generally so as to satisfy the Pauling electroneutrality principle.\textsuperscript{11} Thus the unsaturated metal cations at the surfaces of oxides will tend to be neutralized by OH$^-$ and the unsaturated oxide anions will tend to be neutralized by H$^+$. It is energetically much more favorable for water to be dissociated into H$^+$ and OH$^-$ ions (17 kcal/mol) than into the corresponding radicals (116 kcal/mol). On these ionic crystals the bonds to ionic adsorbates should be highly localized.

One can think of hydroxylation of SrTiO$_3$ or TiO$_2$ surfaces in terms of acid-base reactions. The titanium cations will act as elec-
tron acceptors, and the oxygen anions will act as electron donors.

A cation capable of sharing an electron pair with an adsorbate is a Lewis acid site; the corresponding anion is a Lewis base. Upon adsorption and dissociation of water, the surface cation has an adsorbed OH⁻ on top of it, while the anion and its adsorbed H⁺ appear as a bridge bonded OH between two cations.

Figure 4-2 shows the hydroxylation arrangement which would be expected for a type I (001) surface of SrTiO₃. The existence of these two OH species has been confirmed by infrared spectroscopy for TiO₂, but no work of this type has been done on SrTiO₃.

The hydroxylated surface may be capable of donating or accepting protons, and therefore is a Bronsted-Lowry acid or base. Hydroxylation has thus caused a change in the chemical character of the surface. It has caused a more stable, less polarized surface to form. Depending on the relative strength of the acid and base sites, a surface has a net acid or base character. In the first chapter I defined the point of zero zeta potential or pH_{pzzp}, to be the pH of a solution (usually containing H⁺ and OH⁻ ions) for which the surface charge on an electrode surface is zero. At pH_{pzzp} there is no dipole layer on the surface, and thus no potential drop across the Helmholtz layer. Hydroxylation will likely cause a change of pH_{pzzp}. For example, dehydrated TiO₂ has a pH_{pzzp} of about 4.7, while the hydroxylated surface has a pH_{pzzp} of about 6.0. Apparently this means that acid sites on the bare surface are more strongly neutralized by water than basic sites. By reducing the surface of TiO₂, the pH_{pzzp} of the hydrated surface changes from 6 to 7.4. This surface is rich in Ti³⁺.
and poor in $O^{2-}$. Apparently, $Ti^{3+}$ is adsorbing $H^+$, because the $pH_{pzzp}$ would have decreased if the extra $Ti^{3+}$ adsorbed $OH^-$. This would explain the $Ti-H$ species reported by Knotek. And Knotek claims that the hydrided surface is unreactive with $H_2O$ and $O_2$.\(^{17}\)

The $pH_{pzzp}$ of hydroxylated $SrTiO_3$ is about 8.2, so that the surface is not basic.\(^{16}\) This might be connected with Knotek's observation that $Sr-H$ groups are formed, but $Sr-OH$ groups are not. In any case, this value of $pH_{pzzp}$ corresponds to an upward bending of the bands at the surface. This is because the electron donating ability of the surface is greater than the electron accepting ability, so that adsorbates will tend to draw electrons to the surface and leave a positive space charge layer. It is observed that the work function of $SrTiO_3$ increases upon hydroxylation, while the work function of $TiO_2$ decreases. An increase or decrease of work function implies an upward or downward bending of the bands at the surface, respectively. Thus the chemical character of the surface corresponds to the electronic effects which are observed. This discussion is another way of looking at the reason that $SrTiO_3$ is to be preferred over $TiO_2$ in photodissociation of water, and this model does not refer to redox levels in solution.

In the remainder of this section I will discuss the controversy that exists about the nature of adsorbed water on the surface of $SrTiO_3$. The question is whether the theory and experimental results mentioned so far correlate with observations about adsorption of water.

On the surface of $TiO_2$ water adsorbs both molecularly and dissociatively, as revealed by infrared and thermal desorption spectro-
Molecular water desorbs at about 425 K and dissociated water at about 500 K. The surface is typically not completely covered by OH groups, but this is related to annealing history. The sites not covered by OH are not numerous enough to account for molecular water adsorption, so one must conclude that molecular water adsorbs on the hydroxylated surface. One might expect water to adsorb both dissociatively and molecularly on SrTiO$_3$, but there is some controversy about this. There is only one thermal desorption peak, a broad peak at about 525 K.

Gas phase or solid phase water has three UPS peaks. Henrich, Dresselhaus, and Zieger found that water would adsorb on TiO$_2$ in such a way that two UPS peaks only were seen in the initial stages of adsorption, with a third peak growing in after greater exposure to water. They saw three peaks from the beginning on SrTiO$_3$. Their interpretation was that the two peaks on TiO$_2$ represented the OH groups seen with infrared spectroscopy, and the third peak (together with the previous two) was due to molecular water. But they inferred from the three peaked spectrum on SrTiO$_3$ that only molecular water was adsorbed. This is to overlook the possibility that molecular and dissociative adsorption begin simultaneously on SrTiO$_3$.

Webb and Lichtensteiger and Ferrer and Somorjai found that water would adsorb readily on the Ti$^{3+}$ rich surface of ion bombarded SrTiO$_3$, but would not adsorb readily on the severely annealed (above 1000 K) surface. On the ion bombarded and lightly annealed (875 K for 5 minutes) surface Ferrer and Somorjai found that oxygen from the lattice of SrTiO$_3$ would exchange with oxygen from isotopically
labelled water (H$_2^{18}$O). This is evidence for dissociative chemisorption on the reduced surface. Webb and Lichtensteiger conclude from their studies that non-dissociative adsorption occurs, but do not rule out dissociative chemisorption.

There is evidence for the presence of hydroxylation even on the stoichiometric surface. If a crystal of SrTiO$_3$ or TiO$_2$ is freshly ion bombarded so as to remove several hundred monolayers of the surface, one observes a peak in the UPS spectrum at about 11-12 eV below the Fermi level which corresponds to the OH$^-$ ion, according to Ferrer and Somorjai. This peak is removed by heating the crystal to 750 K for about one minute, and as I will show later in this chapter, water is desorbed during heating. This OH group is a result of the fact that the bulk of these crystals is typically saturated with hydrogen, as pointed out by Knotek.25

Thus it is not necessary for hydroxylation to occur as a result of water adsorption. In experiments of the type described in Chapters 2 and 3 where the crystals were not annealed at high temperature, the surfaces would have been hydroxylated by interstitial hydrogen. Also, the water exposures and temperatures in my experiments were much higher than those of the ultrahigh vacuum studies mentioned above. I will show later in this chapter that the OH peak at 11-12 eV is restored even on stoichiometric surfaces of SrTiO$_3$ by experimental conditions of the exploratory studies. So it is probably safe to conclude that water exists in both dissociated and molecular forms on the surfaces I experimented with. What is unknown is whether the dissociated
water participated in photocatalytic reactions, or merely acted as a substrate for water that did.

In summary, the surfaces of SrTiO$_3$ and TiO$_2$ are different with respect to pH, band bending, the role of strontium, dissociation of adsorbed water, and the effect of annealing and adsorbed water on the surface Ti$^{3+}$ species. The discussion of these differences should give some insight into the different performance of various metal oxides in photoelectrochemistry and photocatalysis. Also, the discussion should show how ultrahigh vacuum surface analytical techniques may be used to investigate photoelectrode materials. The following sections are an extension of the work in this section with emphasis on the surface effects encountered in experiments described in the other chapters.

B. Experimental

In this section I will describe ultrahigh vacuum experiments performed to investigate the surface of SrTiO$_3$ under conditions of water dissociation and methane synthesis experiments described in Chapters 2 and 3.

The crystals used in these studies were all reduced at least to the degree sufficient to cause dark coloration. Without this, SrTiO$_3$ in the transparent state is so insulating that it will charge up severely under electron beam exposure and make electron spectroscopy difficult. Reduction will cause an increase in the Ti$^{3+}$ concentration at the surface, but this is easily removed by chemisorption of gases. The crystals were rough polished as in the other experiments, and were ion bombarded in order to clean them. In some cases they were lightly annealed in order to remove surface water, but in no case were they severely annealed.
The reduction, bombardment, and annealing make these surfaces somewhat different from the uncleaned stoichiometric crystals used in other experiments. But as pointed out in the introduction to this chapter, this will affect only the initial exposure of the surface to experimental conditions, and not the photocatalytic cycle.

The UHV apparatus used for these studies is described elsewhere. All UPS studies were done with He(I) 21.2 eV light. I added to it an external reaction chamber to simulate the high pressure, high temperature conditions found in experiments in the other chapters. The experimental program consisted of cleaning and characterizing a single crystal sample, transporting it to the external chamber, and exposing it to various gases at controlled temperatures and pressures. The gas was then removed, the crystal transported back into the ultrahigh vacuum chamber, and the surface of the crystal and its adsorbates analyzed. It is expected that any chemisorbed species would stay on the surface of the crystal during the act of pumping the gas out of the reaction chamber and moving the crystal. A weakly physisorbed species could desorb, but it would be likely to desorb under an electron beam anyway.

The crystal was mounted on a massive stainless steel holder. Blank experiments showed no thermal desorption from the holder. Cleaning was done by bombarding the crystal with Ar+ ions at 2000 V and several microamps current for 5-15 minutes. A background pressure of $5 \times 10^{-5}$ torr of Ar was established during bombardment, with no pumping. After bombardment, the surface could be heated by rotating it close to a
tungsten filament so that the front surface was about 1 cm from the filament.

C. Results and Discussion

The first class of experiments to be described concern the adsorption of water on the bare surface of SrTiO₃. The adsorption of water is inferred from the existence of a peak in the ultraviolet photoelectron spectrum of SrTiO₃ + water at about 12 eV below the vacuum level. See Figure 4-3. This peak has been identified as resulting from OH, a species or mixture of several species, with some possible negative charge. This peak is found on the freshly argon bombarded surface of SrTiO₃ with background pressures in the 10⁻¹⁰ torr range. It must be due to OH present in SrTiO₃, and not to water uptake. This result agrees with Knotek’s observations of hydrogen (and OH) present in the bulk.

If the crystal is heated, this peak disappears, and water is observed to desorb. In my experiment, a tungsten filament was thoroughly outgassed, and then the crystal was rotated so that it faced the hot filament at a distance of 5-10 mm. In two minutes the crystal's temperature rose to about 650 K. Mass spectroscopy was performed with a UTI 100-C quadrupole mass spectrometer. Water is desorbed from the freshly bombarded crystal at about 525 K. Hydrogen in small amounts desorbs at about 500 K. See Figure 4-4. These amounts were greater than could be due to cracking of water in the ionizer of the mass spectrometer, because this amount is only 1% as great as the mass 18 peak due to water.
Photoelectron counts (arbitrary units)

Electron binding energy (eV)

-18
-16
-14
-12
-10
-8
-6
-4
-2

EF

Before heating
After heating

OH peak before heating

O (2p)_σ peak

O (2p)_π peak
No oxygen was observed thermally desorbing from the crystal in this temperature range.

If the crystal were placed in the external reaction chamber and exposed to 20 torr of water at 375 K for one hour, water in much greater amounts than for the bombarded crystal would desorb at the same temperature 525 K. It was unnecessary to have a noticeable amount of Ti$^{3+}$ on the surface for water to adsorb and create a large UPS peak at 12 eV. Webb and Lichtensteiger claim that the Ti$^{3+}$ poor surface does not adsorb water well, based on a 500 L (1 L = 1 Langmuir = 10$^{-6}$ torr-sec) exposure. Henrich, Dresselhaus and Zieger note that even the Ti$^{3+}$ rich surface of SrTiO$_3$ is unaffected by 10$^6$ L exposure to water, but that this Ti$^{3+}$ is totally removed by 10$^8$ L exposures. It seems that under my experimental conditions the exposures were so great that any barriers to chemisorption were overcome. If the crystal were annealed heavily before exposure to water, the OH peak in the UPS spectrum still appeared after exposure, and water was observed to desorb from the crystal afterwards. With Auger electron spectroscopy one can observe only a slight decrease of the O(516)/Ti(383) peak height ratio when water is desorbed.

The next class of experiments concerns the roles of CO and CO$_2$ in water dissociation and hydrocarbon synthesis. The role of CO in water dissociation was explained in Chapter 2. It was found that CO could act as a poison, and probably affected the platinum's ability to act as a hydrogen recombination catalyst. Its effect on SrTiO$_3$ was unknown, so the following experiments were performed to expand our information. Synthetic reactions, such as the hydrogenation of
CO on platinized or bare SrTiO₃ were shown in Chapter 3 not to be likely. The only reaction seen was the oxidation of CO to CO₂.

The presence of carbon on the surface of SrTiO₃ is indicated in ultraviolet photoelectron spectra by a peak at above 10 eV below the vacuum level. The adsorption of CO or CO₂ will cause this peak to grow, and the desorption of these gases causes this peak to disappear. See Figure 4-5. The correlation of UPS and AES spectra is interesting. Figure 4-6 shows the AES spectrum for SrTiO₃ which had not been exposed to water, but only to CO₂. The presence of carbon in AES is indicated by the peak at 272 eV. Upon heating, the carbon is entirely removed, according to both AES and UPS, indicating that dissociation of CO₂ does not occur in such a way as to leave carbon on the surface.

In the case of CO, the UPS spectrum is similar to the spectrum with CO₂, but CO is easily removed by the electron beam used to stimulate Auger emission. Therefore only a slight amount of carbon is seen in AES when CO is adsorbed on the surface of SrTiO₃. Upon heating, no carbon is left on the surface from CO, just as with CO₂. Therefore because of the ease of desorption of CO, it seems that the CO on the hydroxylated surface of SrTiO₃ is not bound strongly, even compared to the rather weakly bound CO₂ as determined by thermal desorption spectroscopy. Apparently, a portion of the CO is not oxidized until the surface is heated, and the water driven off. Upon heating it is favorable for this portion of the CO to combine with surface oxygen and desorb as CO₂, rather than to dissociate.

CO does adsorb on the freshly bombarded surface of SrTiO₃, and does reduce the concentration of Ti³⁺ on the surface. But I found
Fig. 4-5

Photoelectron counts (arbitrary units)

Binding energy (eV)

$E_F$
Clean crystal

After adsorption of CO$_2$

After heating

Auger electron energy

Fig. 4-6
that CO adsorbs well on the hydroxylated surface, where no Ti$^{3+}$ would exist. Figure 4-7 shows the codesorption curves for SrTiO$_3$ which has been exposed to 1 atm CO and 20 torr H$_2$O at 375 K for 1 hour. The crystal had been cleaned by ion bombardment and heating before the exposure. A small amount of CO desorbs at the same temperature at which water desorbs (525 K), and more CO desorbs along with CO$_2$ at 575 K. When CO$_2$ is adsorbed on the hydroxylated surface, most of it desorbs when water does, at 525 K, with only a small shoulder at 575 K. See Figure 4-8. Thus it appears that a large portion of the CO is oxidized to CO$_2$, but not all. It also appears that the CO$_x$ species adheres to the surface after the surface is substantially dehydroxylated.

Lo found that CO was oxidized to CO$_2$ on the bare, reduced surface of SrTiO$_3$. He also found that the adsorption of CO caused the work function to increase by 0.5 eV, and the adsorption of CO$_2$ caused the work function to increase by 0.5 eV, and the adsorption of CO$_2$ caused the work function to increase by 0.4 eV. The slightly greater figure for CO may be due to reduction of the surface during its oxidation to CO$_2$.

I observed that CO$_2$ adsorbed on the hydroxylated surface of SrTiO$_3$ decreased the work function by about 0.2 eV. But CO adsorbed on the hydroxylated surface increased the work function by about 0.5 eV. In both cases, when the gases were driven off the surface by heating the work function returned to its value before adsorption, to within 0.1 eV. All of these work function measurements were made by measuring changes in the width of the electron energy distribution curves from ultraviolet photoemission spectroscopy. The width was taken to be the
Fig. 4-7

Mass spectrometer signal (arbitrary units)

Temperature (K)

Mass 18 (H₂O)
Mass 28 (CO)
Mass 28
Mass 44 (CO₂)
Mass 44
Mass 44 (CO\(_2\))

Mass 28 (CO)

Mass 18 (H\(_2\)O)

Temperature (K)

Mass spectrometer signal (arbitrary units)
energy difference between the zero energy side of the secondary electron peak and the top of the valence band.

The conclusions that may be drawn from these experiments are as follows. The changes in work function indicate that CO interacts with the wet surface much more strongly than with the dry surface. The dry, reduced surface is oxygen deficient, and thus cannot give up oxygen as easily as the hydroxylated surface. But it appears that the oxidation of CO to CO\textsubscript{2} generates a different species of CO\textsubscript{2} as regards its binding to the surface than the simple adsorption of CO\textsubscript{2}. In the former case the CO\textsubscript{2} is more strongly bound, as indicated by its higher desorption temperature. In the latter case, CO\textsubscript{2} seems to be bound to the surface by the surface water, and desorbs when the water does. The fact that CO causes the bands to bend upwards, as indicated by its raising of the work function, might be of some use in photochemical reactions. However, the higher desorption temperature of CO\textsubscript{2} generated by oxidation of CO indicates that CO might passivate the surface of SrTiO\textsubscript{3}.

The last series of experiments concern the effect of platinum evaporated on SrTiO\textsubscript{3}. Figure 4-9 shows UPS spectra with platinum on SrTiO\textsubscript{3} in large and small amounts. Large amounts means that the titanium (383) peak in AES was barely visible, and small amounts means that the titanium peak was greater than the platinum peaks. See Figure 4-10. When the platinized crystal was exposed to water, the same OH peak that appeared on the bare crystal in UPS would appear, and could be removed by heating. If the platinized crystal were exposed to CO, a large carbon peak appears in the AES spectrum, and is not
Large amount of platinum on SrTiO₃ showing platinum 5d peak

Small amount of platinum on SrTiO₃

Fig. 4-9
Fig. 4-10

AES signal (arbitrary units)

Auger electron energy

Pt

Ti
removed by heating. This indicated dissociation of CO on platinum. The amount of platinum on the surface did not change the nature of these results.

Figure 4-11 shows the thermal desorption spectra for platinized SrTiO$_3$ exposed to 1 atm CO and 20 torr of water at 375 K for one hour. A large CO desorption peak appears at 500 K, which must be due to CO adsorbed on platinum. Thus not all the CO on platinum decomposes. Again, CO$_2$ desorbs only at the higher temperature, 575 K, where CO shows its second desorption peak. This is probably due to CO adsorbed on the partially bare surface of SrTiO$_3$. The relevance of this experiment to the earlier experiments seems to be in the deposition of carbon on the surface of platinum. The fact that CO desorbs at a temperature lower than typical water dissociation experimental temperatures indicates that if it causes poisoning of platinum, it is because of dissociation of CO. Carbon deposits on platinum would slowly be removed by water, or by oxygen, and the rate of such removal would be lowered if the carbon polymerized to graphite.
Fig. 4-11

Mass spectrometer signal

Temperature (K)

Mass 18 (H₂O)
Mass 28 (CO)
Mass 2 (H₂)
Mass 44 (CO₂)
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FIGURE CAPTIONS

Fig. 1-1 Schematic diagram of apparatus for water dissociation experiment. See Figure 2-2 for detailed drawing.

Fig. 1-2 Schematic diagram of electrochemical apparatus for water dissociation. For TiO\textsubscript{2} anode, the applied bias voltage is about .25 V.

Fig. 1-3 Diagram of energy levels in semiconductor and electrolyte showing differences in potential drop across Helmholtz layer with different pH.

Fig. 1-4 Scheme for electron energy densities in redox couples in solution, and at electrode surfaces. Bottom drawing is one possible distribution; the true distribution has not been measured.

Fig. 1-5 Schematic diagram of energy levels in SrTiO\textsubscript{3} and platinum connected ohmically by means of a wire. Energy levels with a superscript zero are those in the materials before connection.

Fig. 1-6 Schematic diagram of flat-band potentials of SrTiO\textsubscript{3} and TiO\textsubscript{2} with reference to the redox levels of H\textsuperscript{+}/H\textsubscript{2} and OH/H\textsubscript{2}O.

Fig. 1-7 Diagram of the potential due to band bending showing differences in shape depending on doping.

Fig. 1-8 Diagram of energy levels in a semiconductor with an n-type bulk and an intrinsic surface.

Fig. 2-1 Diagram of electron densities of states for water adsorbed on reduced SrTiO\textsubscript{3}.

Fig. 2-2 Drawing of scheme of experimental apparatus used for water dissociation and methane synthesis experiments.

Fig. 2-3 Hydrogen accumulation as a function of time for experiments without copper foil.

Fig. 2-4 Hydrogen accumulation as a function of time showing effects of induction period.

Fig. 2-5 Hydrogen accumulation as a function of time for experiments with copper foil.

Fig. 2-6 Hydrogen accumulation as a function of time for typical experiments of two types.

Fig. 2-7 Hydrogen accumulation as a function of time for experiments with and without CO in addition to water in cell.
Fig. 2-8 Hydrogen accumulation as a function of time for different coverages of evaporated platinum on the surface of SrTiO₃.

Fig. 4-1 Schematic diagram of two possible (001) surfaces of SrTiO₃.

Fig. 4-2 Schematic diagram of (001) surface of SrTiO₃ of type I with water dissociatively adsorbed on it.

Fig. 4-3 UPS spectrum of SrTiO₃ after argon ion bombardment, before and after heating.

Fig. 4-4 Codesorption curves for hydrogen and water from freshly bombarded surface of SrTiO₃.

Fig. 4-5 UPS spectra of surface of SrTiO₃ showing peaks due to adsorbed water and carbon.

Fig. 4-6 AES spectra of SrTiO₃ after cleaning (top), after adsorption of CO₂ (middle), and after heating (bottom).

Fig. 4-7 Codesorption curves for water, CO, and CO₂ for SrTiO₃ which had been exposed only to water and CO.

Fig. 4-8 Codesorption curves for water, CO and CO₂ for SrTiO₃ which had been exposed to water and CO₂.

Fig. 4-9 UPS spectra for SrTiO₃ with small and large coverages of evaporated platinum. Peak in upper spectrum is due to platinum d-band.

Fig. 4-10 AES spectra for SrTiO₃ with small and large coverages of evaporated platinum.

Fig. 4-11 Codesorption curves for hydrogen, CO, CO₂ and water adsorbed on platinized SrTiO₃ which had been exposed to CO and water.
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