CHAPTER I

INTRODUCTION

1.1 Nitrous Oxide and Global Warming

$\text{N}_2\text{O}$ is the third most important of the long-lived greenhouse gases (LLGHGs) in global warming terms accounting for 6.2% of the total global radiative forcing. Radiative forcing is a measure of the influence a greenhouse gas has in altering the balance of incoming and outgoing energy in the Earth-Atmosphere system. Although it only comprises 320 parts per billion of the earth's atmosphere, its contribution to global warming is important as it has a global warming potential nearly 300 times greater than that of $\text{CO}_2$.

The largest source of nitrous oxide ($\text{N}_2\text{O}$) is agriculture, driven mainly by the use of synthetic nitrogen fertilisers, but other important sources are fossil fuel combustion, biomass burning, ammonia from livestock manure and from the industrial production of nitric acid and of adipic acid used in nylon manufacture. $\text{N}_2\text{O}$ is also formed in soils and oceans throughout the world by a natural biogeochemical nitrogen cycle: the microbial processes of nitrification of ammonium and denitrification of nitrate. As they are predominantly biogenic in origin, $\text{N}_2\text{O}$ emissions are difficult to estimate, but the quantity of this gas has virtually doubled since the beginning of the industrial age. The concentration of $\text{N}_2\text{O}$ in the atmosphere continues to increase (0.2–0.3% yearly) and this increase appears to be caused mainly by anthropogenic activities.
The elimination of contaminants from waste effluents has become a primary issue due to the consequences to human health. Several methods have been developed to address this problem such as high temperature incineration, amended activated sludge digestion, anaerobic digestion. One of the most successful of such methods have been the supplementary and complementary use of semiconductor photocatalysts. These materials use the energy of electromagnetic radiation to promote the excitation of electrons to the conduction band where they can diffuse to the surface and participate in reduction reactions. These materials also have application in photovoltaics for solar energy conversion, for instance in photo-electrolytic cells, since the pioneer work of Fujushima et al. Another important application is in gas sensor devices, where the variation of the resistivity of the metal oxide with the adsorption of certain molecules is used as a detection mechanism.

1.2 Photocatalytic Reaction as a Method of Purification

\( \text{N}_2\text{O} \) like other impurities of the earth's atmosphere is almost totally transparent to solar radiation. Only a small portion of the energy of solar light is found in the wavelength \( \lambda \leq 200 \text{ nm} \) spectral region where electronically excited states of these molecules can be formed. In other words, most of the energy of the solar flux cannot participate in such direct photochemical reactions [1]. Photocatalysis with visible-light photocatalysts can facilitate the photooxidative degradation of organic pollutants [2]. Photocatalytic reactions [3] use the energy of photons from light sources to activate a catalyst. Upon activation, adsorbed gases, particularly molecular oxygen (\( \text{O}_2 \)), or hydroxide radical (OH\( _- \)) and contaminant species (organic or mineral compounds), can participate in surface-mediated reactions that, under appropriate operating conditions, can produce and desorb product species, notably \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). A photocatalytic reaction generally includes the following processes: when photons have a higher energy than the
semiconductor band gap, they are absorbed, and electrons in the valence band are promoted to the conduction band, leaving positive holes in the valence band. The excited electron is used to reduce substances, while the positive hole is used to oxidize substances on the surface of the photocatalyst. Importantly, by modulating the Red-Ox potential of a photocatalyst, selectivity may be obtained to conduct reduction reactions, oxidation reactions or partial oxidation reactions and many researches are focused on that goal.

Since the discovery by Fujishima and Honda in 1972 [4] of the photocatalytic splitting of water on a TiO$_2$ electrode under ultraviolet (UV) light, enormous research efforts have been devoted to photocatalysis under UV light in the presence of many semiconductors and semiconductor oxides [5] such as TiO$_2$, SnO$_2$, WO$_3$, SiO$_2$, ZrO$_2$, etc. and this topic developed very quickly during the last twenty five years. In the past years, visible light photocatalysis has gained considerable attention, allowing a better use of sunlight spectrum (i.e. 40 – 50 % instead of 4-5% for UV). Researches on photocatalytic methods, while still in progress, have led to many promising applications for environmental purposes. Still many aspects remain to be solved like: photocatalytic efficiency improvement, increased solar energy utilization, suitable form of catalyst, all in turn influencing the economic aspects of this technique.

1.3 TiO$_2$ as a Photocatalyst

TiO$_2$ is known as a semiconductor material which exhibits photocatalytic activity for decomposition of many organic substances under UV light irradiation [6]. Up to now, TiO$_2$ has undoubtedly been proven to be the most excellent photocatalyst for the decomposition of many organics under UV irradiation [7]. When exposed to solar radiation it acts as a catalyst for the photodecomposition of pollutant molecules adsorbed on its surface and the transformation into
non-toxic or less toxic compounds. With nanomaterials, TiO$_2$ photocatalysed oxidation or reduction of many pollutants has become a reality in every day’s life. Incorporation of TiO$_2$ in building materials, glass or surface coatings [8] imparts self-cleaning and depolluting properties to them. Regarding its commercial availability, suitable optical and electronic qualities, chemical stability and non-toxicity, TiO$_2$ seems to be the most convenient candidate for photocatalytic conversion of many mineral and organic compounds and especially for GHGs and other climate forcers. Due to the relatively broad band gap energy of about 3.2 eV, the light absorption of anastase TiO$_2$ takes place in the UV range allowing the absorption of only 4-5 % of solar energy, and resulting in low quanta efficiencies. For this reason, much research is actually focused [9] on broadening the spectrum range, in which TiO$_2$ is capable to absorb visible light, as there is almost 10 times more energy produced by sunlight in the visible than in the UV range. Strategies to induce visible light activity have been reviewed by many authors and abundant literature exists on the subject [2,10,11,12,13,14] that enumerates the various ways by which modified TiO$_2$ or other semiconductors are effective for the degradation of organic or mineral pollutants using the visible range of the solar spectrum.

In consideration of the contribution of N$_2$O towards global warming, a computational study of Photocatalytic reduction of nitrous oxide is worthwhile to gain insight into the reaction mechanism.
CHAPTER II

TiO₂ AND PHOTOCATALYSIS

2.1 Introduction of TiO₂

TiO₂ is a popular material which has wide applications in many different fields: it usually serves as a support substrate for the metal particles in heterogeneous catalysis; its stability makes it a perfect corrosion-protective coating material; its dielectric properties makes it an important material in electronic devices; the semiconductor nature also makes it a potential gas sensor; it is also used as a good white pigment in paint and cosmetics for its high refractive index. In fact, TiO₂ was brought into the field of photocatalysis long time ago since it was found responsible for the ”chalking” of the paints (the organic complex in paint be photodecomposed from TiO₂). However, it did not become the star of the photocatalysis until Fujishima and Honda used it to successfully decompose H₂O [4] in 1972. On one hand, enormous efforts have been devoted to enhance its energy efficiency; on the other hand, it has been widely applied in fields of waste water treatment [15] and air purification [16], self-cleaning [17] and anti-foggy [18] where photocatalytic processes are believed to play important roles. The photocatalysis related issues on TiO₂ can be found in good recent reviews by Fujishima [18] and Henderson [19]. In this chapter, a brief introduction on the geometric structures and electronic properties of TiO₂ will be given followed by the basic principles and key processes of photocatalysis on TiO₂.

2.1.1 Geometric Structure

There are three forms of polymorph TiO₂ in nature: rutile, anatase and brookite. In all three phases of TiO₂, Ti atom is surrounded by six O atoms forming an octahedral. Different
ways of packing the octahedrals result in the three types of crystal structure: in rutile, the octahedral shares apex with neighboring ones, in anatase they share edge, and in brookite they share edge and/or apex. Rutile is the most stable phase as bulk material, the other two forms of TiO$_2$ can transform to rutile when heated to high temperature. But as nanoparticles, the anatase becomes more stable than the rutile. Most studies have been focused on rutile and anatase. Usually, anatase is suggested to have higher chemical activity than rutile. Most commercial products of TiO$_2$ are mixtures of rutile and anatase because the mixed phase usually outperform any of the individual phase.

Rutile is abundant in nature, and it is easy to get large crystal sample of it, which is why most of the studies on the surface involve rutile. According to its Wulf structure the (110) surface is its most thermodynamic stable facet. The rutile (110) surface consists of alternative bridge oxygen (Ob) row and five-fold coordinated Ti (Ti5c) row. Usually, there are bridge oxygen vacancies (Ov) on the surface with a coverage about 6%. The Ov has been shown to be an active center for chemical reactions such as the dissociation of H$_2$O, the adsorption of O$_2$ and the oxidation of CO. For anatase, its most stable facet is the (101) surface that contributes about 90% of the exposed surface for anatase crystal [21]. Different from the rutile (110) surface, the anatase (101) surface is stable and chemically inertial. Oxygen vacancies tend to appear in the subsurface [22], and molecules usually prefer to adsorb associatively on the surface [23].

2.1.2 Electronic Structure

The Ti atom is in the octahedral crystal field created by the six oxygen atoms around it. Therefore, its five degenerate d orbitals split into two groups: the e$_g$ group containing d$_{x^2−y^2}$ and d$_{z^2}$, and t$_{2g}$ group that includes the rest three d orbitals (d$_{xy}$, d$_{yz}$ and d$_{xz}$). The hybridization of the d orbitals with the p orbitals of oxygen atoms produces the material’s electronic structure. Its
conduction band is mostly derived from the d orbitals: the bottom is mainly from e\textsubscript{g} orbitals and higher energy states from t\textsubscript{2g} orbitals. The electronic state on the top of the valence band of TiO\textsubscript{2} is mostly derived from the p orbital of oxygen atoms. Although, d orbital also contributes to the deep valence band, the p orbital character determines the nature of the photoexcited hole and the d orbital determines the nature of the photoexcited electron.

Usually, bulk TiO\textsubscript{2} is an n-type semiconductor, defects such as oxygen vacancy and Ti interstitial atoms could produce gap states below the conduction band. An oxygen vacancy will contribute two and Ti interstitial gives four extra electrons to the system. Depending on the degree of the reduction, the color of TiO\textsubscript{2} can vary from white to dark blue [24]. There have been arguments about the main source of the gap states. Experimental evidences support the coexistence of the oxygen vacancy [25] and Ti interstitial [26]. Therefore, which form of defects dominates seems to depend on the treatment of the material. Near the rutile (110) surface, the oxygen vacancy is usually believed to be the major source; while in the bulk material, theoretical calculations suggested that Ti interstitial could become the dominating contributor only when the temperature is higher than 1500 K [27]. The spatial location of the defect states has also been investigated by several theoretical works. For the oxygen vacancy on the rutile (110) surface, the extra electron was predicted to localize at the under-coordinated Ti atom from the hybrid functional calculations [28]; whereas DFT+U calculations suggested the subsurface Ti atom to be the most favorable site [29]. The difference may come from the different choice of supercell in these two works. In fact, experiments showed that even if the extra electrons are injected by Na atoms, they will still localize at the subsurface Ti atoms [30]. However, the energy difference for trapping at different sites is quite small. And the dynamic simulations have shown that the
electron is quite mobile [31]. It hops between different Ti atoms and with the biggest possibility to appear at the subsurface Ti.

### 2.2 Principles of photocatalysis on TiO2

Photocatalysis is closely related to electrochemistry. The device used by Fujishima and Honda to split the water is similar to an electrochemical cell, in which TiO$_2$ served as the anode and platinum served as the cathode. In electrochemistry, an external bias voltage is usually applied to maintain a potential difference between the anode and the cathode, which allows the oxidation and reduction to happen. Whereas in photocatalysis, such a potential difference is created and maintained by the illuminating light that pumps the electrons in the semiconductor’s valence band to its conduction band. The valence band maximum (VBM) determines its oxidation potential and the conduction band minimum (CBM) determines its possible maximal reduction potential. The external bias is not necessary if the redox potentials of the redox couples are within the band gap of the material. Therefore, TiO$_2$ itself can be used alone and the oxidation and reduction reaction which initiated by the photogenerated hole and electron occurs on different region of it. Sometimes, metal particles are loaded on TiO$_2$ which can serve as a local cathode in the reaction. The electrochemical cell set up is still useful if an external bias is needed to overcome the over potential of the reaction. But in most cases, TiO$_2$ is used alone as in colloidal especially in its applications in various fields (not in solar cell).

As a semiconductor, the valence band of TiO$_2$ is fully occupied and its conduction band is empty. Under UV illumination, the electron in the valence band will be excited to the conduction band within 10 fs [18]. If the energy of the photon is larger than the band gap, the hot electron and hole are created, and they will relax to the band edge at the time scale of sub-picosecond (thermalization). The relaxed electron and hole do not always stay at the band edge.
Three processes can happen: trapping, recombination, and transfer to molecules to initiate reactions (trapped charge carrier can also transfer to molecules). Apparently, the charge transfer process is the core of photocatalysis, many factors affect this process and contributes a lot to the complexity of the photocatalytic reactions. On the other hand, other processes will also greatly affect the performance of the material and the mechanism of the reactions. For example, the excitation determines which part of solar energy that can be harvested by the material; the trapping of the excited charge carriers reduces their mobilities, the nature of the trapped carrier is difficult to be characterized and it is one of the major problems in theoretical study on photoreactions; the recombination will reduce the number of the excited charge carrier and will definitely compromise the performance of the material. From the excitation of charge carriers to the completion of photoreaction, every step needs to be considered to fully understand the mechanism of the reactions. Therefore, each process mentioned above will be discussed in detail in the following sections.

2.2.1 Light Absorption and Excitation

The band gap of TiO₂ is about 3.0 eV, which means it can only absorb the Ultraviolet light that only contributes 4% to the solar light. After the absorption of light, an exciton state, which is a bounded state of the photoexcited electron and hole, is usually formed. It is not very stable and can be easily split by temperature fluctuation and electric field. Therefore, it is difficult to study its lifetime, or characterize its role in photocatalytic reactions. Besides, the photoreaction is usually described by the ‘independent” electron and hole. For example, reactions are referred to be initiated by either electron or hole.

To enhance the light harvest efficiency of TiO₂, much effort has been dedicated to narrow its band gap. Doping of TiO₂ with various non-metal elements such as N, C, B can produce new
states above the VBM [32,33], and doping with metal elements such as Cr, Co and other transition metal will usually produce new states below the CBM of TiO$_2$. Several works showed that co-doping with metal and non-metal elements can greatly extend the light adsorption [33-36] to visible light region. C-doped TiO$_2$ shows a eight-fold enhancement of the photo conversion efficiency [36]; co-doping with W will even outperformed the C-doped TiO$_2$ for water splitting[37]. Yet, the efficiency of the material is still far from satisfaction.

2.2.2 Thermalization

If the energy of the photon is larger than the band gap, the electron on the top of the valence band can be excited to higher energy level above the bottom of the conduction band. Similarly, hot hole can be also created below the top of the valence band. These hot charge carriers have higher reduction (the electron) and oxidation (the hole) power than those at the band edge. If they can stay there, the photocatalytic properties of the material can be tuned by changing the wave length of the illuminating light. Unfortunately, in most cases, the hot electron will relax to the CBM and the hole to the VBM with the energy released as heat. Thermalization of hot electron has usually been studied by injecting them via photoexciting dye molecules and then tracing them from two photon absorption spectra. It was found that the thermalization happens in 10 fs time scale on the rutile (110) surface [38], while it is much slower in the nanoparticle [39] (300 fs). It is harder to study the thermalization of the hole because there is no material can be used to inject hole into TiO$_2$. But some studies indicate that, in some cases, the hole transfer or trapping can precede the thermalization [40, 41]. This suggests that the non-thermalized hole may need to be taken into account in some reactions. The possibility and extend for this to happen is largely dependent on the donor’s redox potential [42].
2.2.3 Trapping

After the thermalization, if the charge carriers stay at the band edge, they will remain delocalized. However, these charge carriers will undergo localization in sub-picosecond after light excitation [43]. The trapped charge carrier appears as a localized state in the band gap [44, 46]. Most photoreactions take place in a time scale range from nanosecond to microsecond, thus, it is believed that they are initiated by the localized charge carriers [18]. It is therefore essentially important to know the nature of the trapped charge carrier. For example, if the trapping energy is too large, the redox power of the electron will decrease significantly; if the electron (hole) is shallowly trapped it will be easily excited back to the conduction band (valence band). On the other hand, trapping helps the separation of the electron and hole, and generally enhances the efficiency; however, if the trapping site is not favourable for the charge transfer to the molecule then it may have a negative influence on the reaction.

Electron paramagnetic resonance (EPR) has been applied frequently to detect the trapped electrons and holes. It was found that the photogenerated electrons and the excess electrons produced from the creation of oxygen vacancy result in the same Ti$^{3+}$ EPR signals [47]. And theoretical calculations on the rutile TiO$_2$(110) surface suggested that the excess electron tends to localize at the subsurface Ti atoms [29]. For the hole, the results are much more controversial. Many candidates have been proposed from EPR experiments. For example, the subsurface oxygen under a surface hydroxyl [48], the terminal oxygen radical [49], the lattice oxygen [50], and the hydroxyl group [51]. Transient adsorption experiments suggested that there are at least two types of trapped hole in anatase [52], the shallow hole in thermal equilibrium with the free hole, and the deep hole. However, the nature of both hole species are unknown. Theoretical
studies suggested that the hole tends to localize at the least-coordinated oxygen atom on the anatase (101) surface [53].

2.2.4 Recombination

Another aspect that influences the activity is the lifetime of the excited charge carriers. The excited electron will recombine with the hole through the radiative and nonradiative channels (the ratio of the two ways is hard to determine), usually the nonradiative channel is the dominate one. Recombination will greatly compromise the performance of the catalyst. To suppress the recombination, we have to know the factors that influence the recombination. However, there is no systematic study on its relation with the type and density of recombination center yet. In principle, both free and trapped electrons can recombine with the free or trapped hole. It was found that on P25 TiO₂, the recombination occurs at the particle interface as the free electron recombines with the trapped hole [54]. Therefore, from photoluminescence, Nakamura et al. proposed that the trapped hole orbital should be at 1.5 eV above the VBM [50]. At the same time, they found that the photoluminescence only happens on the flat surface at the atomic level. This may be the reason why the nonradiative is usually the dominating way of recombination. Du et al. found that the volume to surface area ratio determines [55] the recombination rate because the volume of the particle determines the adsorption and the surface area basically determines the recombination. To suppress the recombination, TiO₂ is usually decorated with metal nanoparticles which will capture the excited electrons. The Schotty barrier is believed to prevent the electrons from jumping back to semiconductor for recombination. Sometimes one type of charge carrier scavenger can be added as sacrifice species to enhance the lifetime of the other type of charge carrier. For example, methanol [56] is usually used as hole scavenger and O₂ and H₂O₂ are efficient in consuming the excited electrons [57].
2.2.5 Charge Transfer

The core of photocatalysis is the transfer of charge carriers to the molecules initiating the reactions. To understand the charge transfer process is to characterize the role of the charge carrier in the reaction. To do so, there are several questions about charge transfer need to be answered: what is the direction of charge transfer and the transfer rate? Is it transferred directly or indirectly? What is the timing of charge transfer? The answers to these questions are closely related to the mechanism of the reactions.
CHAPTER III

THEORETICAL METHODS

3.1 Introduction

The aim of ab initio molecular orbital theory is to predict the properties of atoms and molecules. It is based on the fundamental laws of quantum mechanics. Different mathematical transformations and approximation techniques are necessary to solve the equations that build up this theory. We review this theory briefly.

3.2 The Schrodinger Equation

For an isolated N-electron atomic or molecular system within the Born-Oppenheimer approximation, the electronic Schrodinger equation is given by

$$\hat{H}_{\text{elec}} \Phi_{\text{elec}}(r) = E_{\text{elec}} \Phi_{\text{elec}}(r)$$

where $E_{\text{elec}} = E_{\text{elec}}([R_A])$ is the electronic energy, $\Phi_{\text{elec}} = \Phi_{\text{elec}}([r_i], [R_A])$, is the wave function which describes the motion of electrons and explicitly depends on the electronic coordinates but depends parametrically on the nuclear coordinates, as does the electronic energy. By a parametric dependence we mean that, for different arrangements of the nuclei $\Phi_{\text{elec}}$ is a different
function of the electronic coordinate. $\hat{H}_{\text{elec}}$ is the electronic Hamiltonian operator describing the
motion of $N$ electrons in the field of $M$ point charges:

$$
\hat{H}_{\text{elec}} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N} \frac{1}{r_{ij}}
$$

The total energy $E_{\text{tot}}$ is the electronic energy $E_{\text{elec}}$ including the nuclear repulsion energy according to the following equation:

$$
E_{\text{tot}} = E_{\text{elec}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}
$$

### 3.3 The Hartree-Fock Approximation

The Hartree-Fock approximation\cite{58, 59} is a mean field approximation, where an
electron is thought to move in the average field due to all other electrons present in the system. On the basis of the variation theory, the lowest value of $E$ is approximated as $E_0$ identified as the electronic energy for the selected nuclear configuration

$$
E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle
$$

where $\psi_0 = |\chi_1, \chi_2, …, \chi_N\rangle$ is a single Slater determinant. By minimizing $E_0$ with respect to the spin orbitals, it is possible to derive Hartree-Fock equation, which is basically an eigenvalue equation of the type,

$$
\hat{f}_i(i)\chi_i(x_i) = \epsilon_i \chi_i(x_i)
$$
where the \( \hat{f}_i(i) \) is an effective one electron operator called the Fock operator having the following form,

\[
\hat{f}_i(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + v^{HF}(i)
\]

Here \( v^{HF}(i) \) is the average potential experienced by the i-th electron due to the presence of other electrons in the system. The essence of the Hartree-Fock approximation is to replace the complicated many-electron problem by one electron problem in which the electron-electron repulsion is treated in an average way. The Hartree-Fock potential, \( v^{HF}(i) \), term depends on the spin orbital of other electrons i.e., the Fock operator depends on its own eigenfunctions. Thus Hartree-Fock equation is non-linear and has to be solved iteratively.

The Hartree-Fock calculations can be closed-shell calculations with all paired electrons or open shell calculations with some unpaired electrons. In closed-shell restricted Hartree-Fock (RHF) calculations all the electrons are paired so that the spatial orbitals are doubly occupied. In unrestricted Hartree-Fock (UHF) calculations the orbitals need not be doubly occupied. The HF equations might be solved numerically according to the suggestion of Roothaan and Hall [60, 61]. A set of known spatial basis functions (for example, atomic orbital basis functions) is introduced and the unknown molecular orbitals are expanded in the linear expansion:

\[
\psi_i = \sum_{\mu}^{K} C_{i\mu} \varphi_{\mu}
\]

The problem of calculating the HF molecular orbitals is then reduced to the problem of calculating a set of expansion coefficients. Substituting the above equation into the HF integrodifferential equation therefore gives \( FC = SC\varepsilon \) where \( F, S, C \) and \( \varepsilon \) are Fock matrix,
overlap matrix, square matrix of the expansion coefficients, and the diagonal matrix of the orbital energies $\varepsilon_i$, respectively. For a nice introduction to the theoretical background on these topics, see the book by A. Szabo and N. S. Ostund [62]

3.4 Density Functional Theory

In DFT [63], the density of the system is taken as the basic variable. The Hohenberg-Kohn (HK) theorem I and II set the base stone of DFT. According to HK theorem I, the external potential ($V_{ext}$) of any interacting system is uniquely determined by its ground state particle density to a constant. Once the $V_{ext}$ is determined, the Hamiltonian of the system and all the properties of the system are determined by only the ground state density $\rho$. The HK theorem II says that for any $V_{ext}$, it exists a universal functional $F[\rho]$ such that the energy functional:

$$E[\rho] = F[\rho] + \int \rho(\mathbf{r}) V_{ext} d\mathbf{r}$$

$$F[\rho] = T[\rho] + V_{ee}[\rho]$$

obtain its minimum at the the ground state density. The problem is that the exact form of $F[\rho]$ is unknown. To be able to apply the theory to real system, Kohn and Sham introduced a non-interacting system that has the same density with the interacting system as a reference [64]. Its kinetic energy can be written as:

$$Ts[\mathbf{r}] = \sum_i \langle \phi_i(\mathbf{r}) | - 1/2 \nabla^2 | \phi_i(\mathbf{r}) \rangle \rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

where $\phi_i(\mathbf{r})$ is called Kohh-sham orbital, then the energy functional of the interacting system can be recast as:

$$E[\rho] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + Ts[\rho] + J[\rho] + Exc[\rho]$$

where, $J[\rho] = 1/2 \int \rho(\mathbf{r})\rho(\mathbf{r})/|\mathbf{r} - \mathbf{r}'|d\mathbf{r}$ is the Coulomb interaction, and $Exc[\rho] = (T[\rho] - Ts[\rho]) + V_{ee}[\rho] - J[\rho]$ is the exchange-correlation energy.
The variation of the $\text{Exc}$ to $\rho$ is called the exchange-correlation functional:

$$V_{xc} = \delta\text{Exc}/\delta\rho(r)$$

Kohn-Sham equation which governs the Kohn-Sham orbital can be derived via the variation principle:

$$[-1/2\nabla^2 + V_{\text{Ext}}(r) + V_{\text{Coul}}(r) + V_{xc}(r)]\phi_i(r) = \epsilon_i\phi_i(r)$$

where the

$$V_{\text{Coul}}(r) = \int \rho(r) |r - r'| dr'$$

Therefore, once we know the $V_{xc}$, the Kohn-Sham orbital can be obtained by solving the Kohn-Sham equation in self-consistent field method. The Kohn-Sham orbital can then be used to get the density and the energy of the interacting system. It seems that we are replacing the question of finding the $F[\rho]$ with the problem of finding $V_{xc}$. However, the $V_{xc}$ can be constructed from other ways. For example, for homogeneous electron gas, the exchange and correlation are local. Kohn-Sham suggested to use it to approximate the real system’s $V_{xc}$. It has been proved to be a big success for solid state. But DFT has still problems, such as overestimating the bonding energy, self-interaction error, band gap problems and so on. To improve the $V_{xc}$, the density gradient and other high order terms such as the Laplacian of the density and/or the kinetic energy density and so on [65] should be included into $V_{xc}$. It is worth noting that the Kohn-Sham orbital is not real molecular orbital, but it is usually a good approximation of it. The energy levels and shapes of the Kohn-Sham orbitals usually agree well with those from various methods.

3.5 Basis-sets

Quantum chemical calculations for atoms and molecules are performed using linear combination of atomic orbitals-molecular orbitals (LCAO-MO)
\[ \psi_i = \sum_{\mu} C_{i\mu} \varphi_{i\mu} \]

where \( \psi_i \) is the \( i \)-th molecular orbital, \( C_{i\mu} \) are the coefficients of linear combination, \( \varphi_{i\mu} \) is the \( \mu \)-th atomic orbital, and \( n \) is the number of atomic orbitals. This term may also be replaced by ‘basis functions’. An example for such function are Slater Type Orbitals (STO’s) [66], that were used due to their similarity to the atomic orbitals of the hydrogen atom. They are described by a function depending on spherical coordinates:

\[ \varphi(\zeta, n, l, m; r, \theta, \phi) = N r^{n-1} e^{-\zeta} Y_{ln}(\theta, \phi) \]

where \( N \) is a normalization constant, \( \zeta \) is called exponent, \( r, \theta \) and \( \phi \) are spherical coordinates, \( Y_{ln} \) is the angular momentum eigenfunction and \( n, l \) and \( m \) are the principal quantum number, angular momentum quantum number and magnetic quantum number respectively. Unfortunately, functions of this kind are not suitable for a convenient and fast evaluation of the two-electron integrals. That is why the Gaussian type orbitals (GTO’s) [67] were introduced. One can approximate the shape of the STO function by summing up a number of GTOs with different exponents and coefficients. The GTO is expressed as:

\[ \varphi(\zeta, n, l, m; x, y, z) = N x^n y^l z^m e^{-\alpha r^2} \]

where \( N \) is a normalisation constant, \( x, y \) and \( z \) are cartesian coordinates, and \( n, l \) and \( m \) are simply integral exponents in Cartesian coordinates, which are completely different from the same notations used in STOs and \( r^2 = x^2 + y^2 + z^2 \).
For quantum chemical calculations, a linear combination of Gaussian primitives is usually used as basis functions. Such functions will have their coefficients and exponents fixed. These are called Contracted Gaussian Type orbitals (CGTO). Obviously, the best results could be obtained if all coefficients in such Gaussian expansions were allowed to vary during molecular calculations. However, the CPU time requirements are more acute. The first Gaussian contractions were obtained by a least square fit to Slater type atomic orbitals. In the minimal basis set (i.e., single zeta (SZ); the numbers of zeta ($\zeta$) is $N = 1$) only one basis function (contraction) per Slater type atomic orbital is used. Double zeta (DZ) sets ($N = 2$) have two basis functions per orbital, etc. Since valence orbitals of atoms are more affected by forming a bond than the inner (core) orbitals, more basis functions were assigned to describe valence orbitals. This prompted the development of split-valence (SV) basis sets, i.e., basis sets in which more contractions are used to describe valence orbitals than core orbitals. Frequently, the core orbitals are extensive contractions consisting of many primitive Gaussians to represent the ‘cusp’ of s-type functions at the position of the nucleus reasonably well. The ‘zeta’ terminology is often augmented with a number of polarization (P) functions. Thus, DZP means double-zeta plus polarization, TZP stands for triple-zeta plus polarization, etc. Occasionally the number of polarization functions is given explicitly, e.g., TZDP, TZ2P, TZ+2P stands for triple-zeta plus double polarization. The letter V denotes split valence basis sets, e.g., DZV represents basis set with only one contraction for inner orbitals, and two contractions for valence orbitals. The notation adopted by Pople and co-workers emphasizes also on the nature of split valence basis sets (SV), resulting in the general notation-scheme n-ijG or n-ijkG, which can be decoded as: n-number of primitives for the inner shells, ij or ijk-numbers of primitives for contractions in the valence shell. Pople’s basis sets can also be augmented with d-type polarization functions on
heavy atoms only (n-ijG(d) or n-ijkG(d)) or on all atoms, with additional p-functions on hydrogen (n-ijG(d,p) or n-ijkG(d,p)). The polarization functions are important for reproducing chemical bonds. Basis sets are also frequently augmented with diffuse functions. Such Gaussian functions have very small exponents and decay slowly with the distance from the nucleus. Diffuse functions are necessary for a correct description of anions and weak bonds (e.g., hydrogen bonds) and are frequently used for calculation of various properties (e.g., dipole moments, polarizabilities, etc.). The notation is widely used: n-ij+G or n-ijk+G when one diffuse s-type or p-type function is added to standard basis set on heavy atoms. In this case the s-type or p-type functions have the same exponents.

3.6 Geometry optimizations

The way the energy of a molecular system varies with small changes in its structure is specified by its potential energy surface. A potential energy surface is a mathematical relationship linking molecular structure and the resultant energy. For a diatomic molecule, it is a two-dimensional plot with the internuclear separation on the X-axis (the only way that the structure of such a molecule can vary), and the energy at that bond distance on the Y-axis, producing a curve. For larger systems, the surface has as many dimensions as there are degrees of freedom within the molecule.

Geometry optimizations usually attempt to locate minima on the potential energy surface, thereby predicting equilibrium structures of molecular systems. Optimisations can also locate transition structures. At both minima and saddle points, the first derivative of the energy, known as the gradient, is zero. Since the gradient is the negative of the forces, the forces are also zero at such a point. A point on the potential energy surface where the forces are zero is called a
stationary point. All successful optimizations locate a stationary point, although not always the one that was intended.

A geometry optimization begins at the molecular structure specified as its input, and steps along the potential energy surface. It computes the energy and the gradient at that point, and then determines how far and in which direction to make the next step. The gradient indicates the direction along the surface in which the energy decreases most rapidly from the current point as well as the steepness of that slope.

Most optimization algorithms also estimate or compute the value of the second derivative of the energy with respect to the molecular coordinates, updating the matrix of force constants. These force constants specify the curvature of the surface at that point, which provides additional information useful for determining the next step.
4.1 Introduction

In this work we try to investigate the possible mechanism of the reduction of N\textsubscript{2}O using TiO\textsubscript{2} as the photocatalyst. We limit our study to rutile, the most common polymorph of TiO\textsubscript{2}. According to the Wolf structure, the (110) surface is the most thermodynamic stable facet of rutile. The rutile (110) surface consists of alternative bridge oxygen row and five-fold coordinated Ti row. Usually, there are bridge oxygen vacancies (O\textsubscript{v}) on the surface with a coverage about 6%. The O\textsubscript{v} has been shown to be an active centre for chemical reactions.

4.2 Mechanism for the Reaction

We assume that the reaction involves the following steps.

1. Adsorption of N\textsubscript{2}O on the oxygen vacancy
2. N-O bond breaking
3. Desorption of N\textsubscript{2} molecule

We use Gaussian 09 package [68] for doing the computation. Since the computation is difficult for a three dimensional crystal, we modeled the surface by taking only one layer
containing five Ti atoms nine oxygen atoms and one oxygen vacancy. N$_2$O molecule is assumed to be adsorbed with the oxygen atom occupying the position of oxygen vacancy. We tried for a geometric optimization, but it could not be obtained. Hence we tried for single point energy calculation using the N-N and N-O distance as in optimized structure for N$_2$O molecule. Ti-O distance is assumed to be a in the rutile crystal.

Parameters used for the Z-Matrix

![Z-Matrix diagram](image)

The energy is found to be equal to -5108.628222 hartrees

To calculate the activation energy we have to get the transition state. As in the case of ground state, the structure corresponding to the transition state also could not be optimized. Hence we did extensive calculations using the ‘scan’ option in Gaussian. We calculated energies corresponding to different N-O an N-N distances and obtained the maximum energy in the minimum energy path. The structure with O-N distance 1.88Å and N-N distance 1.11Å is considered to be the transition state whose energy is found to be -5108. 53053 hartrees. Thus the activation energy will be equal to -5108. 53053-(-5108.628222)= 0.097692 hartrees = 2.658336 eV. This amount of energy can be easily transferred since the band gap in rutile is 3.2 eV.
**Input for computing energy of the ground state**

```plaintext
# B3LYP /6-31g(d) Test
TiO2
0 1
Ti
Ti  1  3.56396145
    Ti  2  6.487  1  24.483204
    Ti  2  7.1279229  3  24.483204  1  0.00000000
    Ti  4  6.487  2  24.483204  3  180.00000000
    O  1  1.983  2  90.0  3  90.0
    O  1  1.946  2  24.483204  3  0.0
    O  1  1.946  4  24.483204  3  180.0
    O  1  1.946  3  24.483204  2  0.0
    O  1  1.946  5  24.483204  4  0.0
    O  2  1.96597  5  90.0  3  180.0
    O  4  1.96597  3  90.0  2  180.0
    O  3  1.96597  4  90.0  5  180.0
    O  5  1.96597  2  90.0  3  180.0
    O  1  1.983  2  90.0  3  -90.0
    X  15  1.0  1  90.0  9  0.0
    N  15  r  16  90.0  6  180.0
    X  17  1.0  1  90.0  9  0.0
    N  17  rn  18  90.0  6  180.0

Rn = 1.13431
r = 1.19249
```
4.3 Reaction in the absence of TiO$_2$

To obtain the activation energy for the reaction in the absence of TiO$_2$ we optimized the structure for N$_2$O and N$_4$O$_2$. There was one imaginary frequency for the latter, suggesting that it may be the transition state.

Energy corresponding to the ground state (2N$_2$O) \(-367.360243\)

Energy corresponding to the transition state (N$_4$O$_2$) \(-367.0965132\)

Activation energy \(= 0.637298\) hartees which is a very large value.

Thus the reaction cannot take place in the absence of TiO$_2$ at ordinary temperature.

**Input for the ground state of N$_2$O**

#T B3LYP/6-31G(D) Opt Freq Test

N2O

0, 1
N
X 1 1.0
N 1 nn 2 90.0
O 1 no 2 90.0 3 180.0

nn=1.145
no=1.12
**Input for the Transition state**

#T RHF/6-31G(D)  Opt Freq Test

N2O ts

0,1
O
O 1 oo
X 1 1.0 2 90.0
N 1 no 3 90.0 2 d1
N 2 no 3 90.0 1 d1
N 4 nn 1 nno 2 d
N 5 nn 2 nno 1 -d

oo=1.1
no=1.2
nn=1.0
nno=150.0
d1=90.0
d=180.0

**4.4 Conclusion**

In summary, we have investigated systematically the molecular mechanism for the photocatalytic reduction of N₂O using rutile. The N₂O molecule first adsorbs at the oxygen vacancy. The energy obtained by the absorption of photon is transferred to the complex and the N-O bond breaks with the liberation of N₂ gas.
REFERENCES

66. J.C. Slater, Phys. Re.36 1930, 36, 75.