A FIRST PRINCIPLE STUDY OF CHEMICAL ACTIVITY ON PdO(101) THIN FILM SURFACE

By

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UNIVERSITY OF FLORIDA

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To Priyanka, Caitlyn, my parents, brother, and my in-laws.
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<tr>
<td>$\Psi$</td>
<td>Electronic wave function</td>
</tr>
<tr>
<td>$\hat{H}$</td>
<td>Hamiltonian operator</td>
</tr>
<tr>
<td>$E$</td>
<td>Eigenvalue</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Plank's constant</td>
</tr>
<tr>
<td>$m_e$</td>
<td>Electron mass</td>
</tr>
<tr>
<td>$r$</td>
<td>Spatial position of an electron</td>
</tr>
<tr>
<td>$\Psi_n$</td>
<td>Individual electron wave function</td>
</tr>
<tr>
<td>$n(r)$</td>
<td>Electron density</td>
</tr>
<tr>
<td>$E_{XC}$</td>
<td>Exchange-correlation functional</td>
</tr>
<tr>
<td>$V_H$</td>
<td>Hartree potential</td>
</tr>
<tr>
<td>$V_{XC}$</td>
<td>Exchange-correlation potential</td>
</tr>
<tr>
<td>$\hat{H}$</td>
<td>Hamiltonian operator</td>
</tr>
<tr>
<td>$E_{HF}^{\text{HF}}$</td>
<td>Hartree-Fock exact exchange functional</td>
</tr>
<tr>
<td>$E_{\text{known}}[[\Psi_i]]$</td>
<td>Electron kinetic energies + coulomb interaction between electrons and nuclei, between pairs of electrons and between electrons and nuclei</td>
</tr>
<tr>
<td>$E_{XC}[[\Psi_i]]$</td>
<td>Exchange-correlation functional</td>
</tr>
<tr>
<td>$V$</td>
<td>Interaction potential between an electron and collection of nuclei</td>
</tr>
<tr>
<td>$V_H$</td>
<td>Hartree potential, coulomb repulsion between specific electron and total electron density</td>
</tr>
<tr>
<td>$V_{XC}$</td>
<td>Potential describing exchange and correlation contributions</td>
</tr>
<tr>
<td>$\nabla n(r)$</td>
<td>Gradient of the electron density</td>
</tr>
<tr>
<td>$E_{\text{nl}}$</td>
<td>Non-linear exchange</td>
</tr>
<tr>
<td>$E_{\text{vdW}}$ and $E_{\text{disp}}$</td>
<td>van der Waals/dispersion energy (may even be in a DFT-D3 relaxed configuration)</td>
</tr>
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</table>
\( F_{vdW} \) and \( F_{disp} \) van der Waals/dispersion force (may even be in a DFT-D3 relaxed configuration)

\( \sigma \)-complexes Sigma complex, predominantly comprises of dative interaction with the surface

\( \eta^2 \) \textit{eta} 2 interaction; where methyl group saddles atop \textit{cus}-Pd atom with two H atoms and a C atom interacting with \textit{cus}-Pd

\( \eta^1 \) \textit{eta} 1 interaction; where methyl group leans atop \textit{cus}-Pd with a H atom and a C atom interacting with \textit{cus}-Pd

\( E_{molec,ads} \) Energy of adsorbed molecule without considering the surface

\( E_{molec,gas} \) Energy of isolated gas-phase molecule

\( r_{AB}^{-n} \) \( n \)th order inter-nuclear distances

\( C_{n}^{AB} \) Dispersion coefficients

\( s_n \) Scaling factor

\( f_{d,n}(r) \) Damping function

\( E \) and \( E_{ads} \) Adsorption/binding energy

\( E_A \) Activation energy for desorption or desorption energy

\( E_{iso} \) Total energy of isolated molecule

\( E_{bare} \) Total energy of bare surface

\( E_{chemisorb} \) Total energy of chemisorbed molecule/surface system

\( \Delta E^{TS} \) Internal energy change of activation

\( \Delta ZPE \) Zero-point energy difference between transition state and initial adsorbed state

\( \Delta E_v \) Change in average vibrational energy

\( R \) Universal gas constant

\( T \) Temperature

\( E_{A,exp} \) Desorption energy estimated experimentally
\( E_{\text{DFT}} \)
- Binding energy estimated by conventional DFT

\( E_{\text{A,DFT}} \)
- Desorption energy estimated by conventional DFT

\( E_{\text{DFT-D3}} \)
- Binding energy estimated by dispersion-correction DFT

\( E_{\text{A,DFT-D3}} \)
- Desorption energy estimated by dispersion-correction DFT

\( E_{\text{elec}} \)
- Energy from electronic interactions in DFT-D3 relaxed configuration

\( E_{\text{dft}} \)
- Energy determined by conventional DFT electronic relaxations

\( F_{\text{dft}} \)
- Force determined by conventional DFT electronic relaxations

\( E_{\text{dft-d3}} \)
- Total energy considering conventional DFT and dispersion effects
  \( (E_{\text{dft-d3}} = E_{\text{dft}} + E_{\text{disp}}) \)

\( F_{\text{dft-d3}} \)
- Total ionic force considering conventional DFT and dispersion effects
  \( (F_{\text{dft-d3}} = F_{\text{dft}} + F_{\text{disp}}) \)

\( \Delta E_{d,i}^\ast \)
- Desorption energy barrier

\( \Delta E_{r,i}^\ast \)
- Reaction energy barrier

\( E_{\text{app}} \)
- Apparent energy barrier for reaction
  \( (E_{\text{app}} = \Delta E_{d,i}^\ast - \Delta E_{r,i}^\ast) \)

\( y_i \)
- Probability that a molecular specie is adsorbed in molecular state \( i \)

\( k_{d,i} \)
- Desorption rate coefficient

\( k_{r,i} \)
- Reaction rate coefficient

\( K_i \)
- Adsorption equilibrium constant

\( q_t^{2D} \)
- Two-dimensional translational partition function of gas-phase molecule

\( q_r \)
- Three-dimensional rotational partition function of gas-phase molecule

\( q_{\text{vib}(g)} \)
- Vibrational partition function of gas-phase molecule

\( q_{\text{ad},i} \)
- Partition function for adsorbed state

\( q_i^\ast \) and \( q_{\text{TS}} \)
- Partition function for transition state
$l_{d,i}$  Statistical factor for desorption  

$l_{r,i}$  Statistical factor for reaction  

$I_j$  Moment of inertia for rotation about principal axis $j$  

$\nu_j$  Frequency of normal mode $j$  

$q_{t}^{1D}$  One-dimensional translational partition function of gas-phase molecule  

$q_{r}^{1D}$  One-dimensional rotational partition function of gas-phase molecule  

$q_{t}^{2D}$  Two-dimensional translational partition function of gas-phase molecule  

$q_{vib}^{3N-2}$  Partition function for adsorbed state with $3N-2$ modes treated as harmonic  

$\nu_d$ and $\nu_{d,i}$  Kinetic pre-factor for desorption  

$\nu_r$ and $\nu_{r,i}$  Kinetic pre-factor for reaction  

$S_r$  Total dissociation probability  

$[RH]_i(T)$  Concentration of molecular state $i$ determined at temperature $T$ from numerical integration of state $i$ mole-balance equation  

$[RH]_i(T + \Delta T)$  Concentration of molecular state $i$ used as input for the numerical integration subsequent temperature step.  

$\alpha$  Molecular adsorption probability
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<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
</tr>
<tr>
<td>CUS / 3F</td>
<td>Coordinatively unsaturated or threefold</td>
</tr>
<tr>
<td>CS / 4F</td>
<td>Coordinatively saturated or fourfold</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent field</td>
</tr>
<tr>
<td>LDA</td>
<td>Local density approximation</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
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<td>PW91</td>
<td>Perdew-Wang 1991 functional</td>
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<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof functional</td>
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<td>Tao-Perdew-Staroverov-Scuseria functional</td>
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<tr>
<td>DDEC</td>
<td>Density derived electrostatic and chemical charge analysis</td>
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<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>NEB</td>
<td>Nudged elastic band</td>
</tr>
<tr>
<td>MEP</td>
<td>Minimum energy pathway</td>
</tr>
<tr>
<td>IS</td>
<td>Initial state</td>
</tr>
<tr>
<td>TS</td>
<td>Transition state</td>
</tr>
<tr>
<td>FS</td>
<td>Final state</td>
</tr>
<tr>
<td>TM</td>
<td>Transition-metal</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna <em>ab initio</em> simulation package</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
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</tr>
<tr>
<td>TPRS</td>
<td>Temperature programmed reaction spectroscopy</td>
</tr>
<tr>
<td>DFT-D</td>
<td>Density functional theory with dispersion</td>
</tr>
<tr>
<td>DFT-D3</td>
<td>Density functional theory with third gen. dispersion treatment</td>
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<td>Quantum mechanical</td>
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<td>ST</td>
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<td>FL</td>
<td>Flat-lying</td>
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<tr>
<td>SXRD</td>
<td>Surface X-ray diffraction</td>
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<td>LEED</td>
<td>Low energy electron diffraction</td>
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A FIRST PRINCIPLE STUDY OF CHEMICAL ACTIVITY ON PdO(101) THIN FILM SURFACE

By

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Major: Chemical Engineering

The chemisorption, activation and dissociation kinetics of \( n \)-alkanes on PdO(101) surface have been studied employing conventional and dispersion-corrected \textit{ab initio} density functional theory (DFT). Adsorption and coverage effects of CO\(_2\) on PdO(101) have also been investigated using dispersion-corrected DFT. These first principle based studies are seen to be consistent with ultra-high vacuum (UHV) experimental predictions and thus enable better interpretation of events at the atomic level on PdO(101) surface.

DFT demonstrates that on PdO(101) surface, \( n \)-alkanes form \( \sigma \)-complexes comprising of strong dative interactions between methyl groups and coordinatively unsaturated (\textit{cus}) Pd atoms. Lower alkanes are seen to favor the stronger but more sensitive \( \eta^2(\text{H,H}) \) dative interaction, while propane and higher alkanes due to steric hindrances and staggering effects on the surface, adopt weaker and lesser sensitive \( \eta^1(\text{H}) \) interactions. The dative interactions weaken surface interacting C-H bonds and thus serve to electronically activate these bonds. Hence the adsorbed \( \sigma \)-complexes play a general role as precursors in \( n \)-alkane activation on the metal oxide surface.
Compared to conventional DFT, dispersion-corrected DFT (DFT-D3) predicts alkane binding energies on PdO(101) that better agree with experimental estimates. Furthermore, the apparent C-H bond cleavage barriers predicted by DFT-D3 are more realistic. Besides determining the pathways for initial C-H bond cleavage of methane, ethane and propane on PdO(101), the dehydrogenation of resulting CH₃ groups from methane initial activation has also been investigated. Methoxy (CH₃O) formation is seen to be energetically more demanding. For propane on PdO(101), DFT-D3 predicts strong preference for the cleavage of primary C-H bond; in agreement with experimental observations. The preference is attributed to greater population of primary bound $\eta^1$ propane configurations on the surface and more stabilizing distribution within the 1-propyl transition state structures.

The dissociation kinetics associated with methane, ethane and propane on PdO(101) has been investigated using micro-kinetic models. Better agreement with estimates from literature and experiments is observed with a $3N-2$ model, where two frustrated adsorbate motions are treated as free motions instead of harmonic approximation. The micro-kinetic simulations demonstrate the importance of accurately describing entropic contributions in kinetic simulations of alkane dissociative chemisorption.
CHAPTER 1
INTRODUCTION

1.1 Background and Motivation

The role of catalysts in industrial chemical processes has been increasing over the last decades as the manufacturing of several significant chemical involves catalysis. Furthermore, biochemically significant processes that have gained popularity recently are observed to be mostly catalyzed. By definition, catalyst is a substance that influences the rate of a reaction without being consumed. However, based on how a catalyst operates, it phase relative to a substrate and whether it promotes or inhibits a reaction, catalytic reactions can be broadly classified as auto or induced, homogeneous or heterogeneous and positive or negative catalysis. Since the type of catalyst influences the overall efficiency and performance of a chemical manufacturing process, development of catalysts that ensure both high activity and precise selectivity is a field of active research.

Industries tend to prefer heterogeneous catalysis where solid catalysts catalyze gaseous or liquid reactants. This preference of heterogeneous over homogeneous catalysts is due to their better adaptability into chemical processes, lower implementation costs and since being in solid form as porous pellets or wire meshes can be easily separated from the reaction system.¹ Late transition metals (especially Ru, Rh, Ir, Pd and Pt) play a substantial role as heterogeneous catalysts in several industrially relevant oxidation processes such as exhaust gas remediation in automobiles and power plants,² ³ catalytic combustion of natural gas,⁴ ⁶ fuel cell catalysis⁷ and selective oxidation of organic compounds.⁸ However, studies attribute the exceptional activity of these metals to the formation of their corresponding oxides in
oxygen rich environments during the reaction processes. Oxide surfaces display an activity completely different compared to the bulk oxide phase. Compared to the original metal, oxide layer represents an entirely new surface with different chemical properties that may dramatically improve the performance of the catalyst. Thus over the last decade, metal oxides have transitioned from being mere support materials for catalysts to actively engaging in catalysis.

Surprisingly, with regards to late transition metal oxide surfaces, there are only a few researchers working on characterizing and understanding their growth and surface properties, especially at the atomic level. The challenge is in the development of well-defined oxide surfaces for characterization in ultra-high vacuum (UHV) and for *in situ* techniques. This is due to late transition metals being resistant to oxidation and the low thermodynamic stability of late transition metal bulk oxides compared to earlier transition metals. Bulk oxide formation of late transition metals (Rh, Ir, Pd and Pt) display a lower exothermicity that translates to high kinetic barriers for conventional oxidizing technique based on dissociative chemisorption of O$_2$. However, these barriers can be overcome by the use of aggressive oxidants such as NO$_2$, O$_3$, atomic oxygen$^{12-14}$ or high-pressure cells.$^{15}$ It is to be noted that among the late transition metals, Ru is an exception as well defined RuO$_2$(110) films can be generated through exposure of Ru crystal to O$_2$ at pressures of $\sim 10^{-3}$ Torr.$^{16-18}$

A high quality PdO(101) thin film can be generated in ultra-high vacuum (UHV) through atomic oxygen beam exposure of a Pd(111) surface.$^{19-21}$ Compared to bare Pd(111) metal surface and bulk PdO layer, PdO(101) surface presents an entirely different chemistry as it comprises of more type of atoms based on atomic specie and
coordination. Coordinatively unsaturated (cus) Pd and O atoms on PdO(101) and bound to three neighboring atoms while coordinatively saturated Pd and O atoms have a four-fold (4f) coordination. Studies identify the coordinatively unsaturated metal and oxygen sites to be key players for enhanced molecular chemisorption and reactivity of late transition metal oxide surfaces as they present a coordination vacancy.\textsuperscript{22, 23} Besides coordination characteristics, the relatively weak metal-oxygen bonding observed in general for late transition metal oxides\textsuperscript{24} facilitate oxidation of chemisorbed species accompanied with reduction of the oxide surfaces. Hence, late transition metal oxide surfaces present and effective phase for promoting oxidative transformations of various compounds. Among late transition metal oxides, both RuO\textsubscript{2}(110) and PdO(101) surfaces are being extensively investigated over the past few years as the experimental techniques for their generation is well established.\textsuperscript{18, 25}

North America has a huge natural gas reserve with methane composition of 70-90\% and 10-30\% for ethane, propane and butane. Recognizing this reserve as a significant energy source or even feedstock for manufacturing higher complex organic chemicals, activating methane has become the holy grail of catalysis. PdO(101) has attracted significant interest because of the observed high activity of various molecular compounds especially alkanes on this oxide surface.

With the realization of numerous compositional combinations for heterogeneous catalysts, traditional trial-and-error methods for catalyst design are becoming insufficient and ineffective. This is where fundamental surface science studies, particularly that utilizing first-principles method is advantageous. Over the last decade first-principles method has become popular as an effective and efficient mean for designing and
developing novel catalytic materials. First-principles method in conjunction with ultra-high vacuum (UHV) experiments enable investigating activity of specific molecular species on a surface and provides a detailed understanding of specific steps in a complex reaction pathway independent of other chemical species that may be present in high pressure environment. Thus a combination of computational quantum chemical calculations and experimental UHV fundamental science studies enable better interpretation of atomic level events on a surface.

1.2 Density Functional Theory

Density functional theory (DFT) is a powerful and commonly used computational quantum mechanical modeling approach that computes electronic structure of matter (many-body systems) and helps in predicting properties of isolated molecules, bulk solids (metals, semiconductors and insulators), fluids (classical and complex) and material interfaces including surfaces. The term 'density functional theory' comes from the use of functionals (functions of another function) of electron density to determine properties of many-electron systems. Since 1990, DFT has gained significant popularity with its better agreement with experimental observations due to the refinement in various approximations of the theory that enable better modeling of exchange and correlation interactions. Furthermore, lower computational cost compared to traditional many-electron wave function based techniques such as Hartee-Fock and Post-Hartee-Fock methods makes DFT even more attractive. A few notable accomplishments of DFT are, explaining the catalytic synthesis of NH₃ on Ru nanoparticles, describing the embrittlement of copper by traces of Bi impurities and probing under extreme conditions the material properties of bulk MgSiO₃ which is an important mineral for
planet formation. The principles behind the functioning of DFT are briefly discussed in the following sections.

**1.2.1 Schrödinger Equation**

The time dependent Schrödinger equation is a partial differential equation that describes the spatial shape and the temporal evolvement of a wave function in a given potential and for given boundary conditions. Substituting time-dependent wave function \( \Psi(x, t) \) with \( \Psi(x) e^{-iEt/\hbar} \) (for 1-dimensional) yields the time-independent Schrödinger equation that is shown in Equation 1-1.

\[
\hat{H} \Psi = E \Psi
\]  

(1-1)

The Schrödinger equation is an eigenvalue problem where \( \Psi \) is a set of eigenstates with a particular set of eigenvalues \( E_n \) that is associated with a particular solution \( \Psi_n \). \( \hat{H} \) is the Hamiltonian operator, definition of which depends on nature of the system being studied. To describe properties of a collection of atoms that comprise a molecule or a bulk solid, the energy of these atoms and energy change associated with atom rearrangement is to be known. This is determined from interactions between subatomic particles namely, positively charged nuclei and negatively charged electrons. Since mass of a proton or neutron is roughly 1800 times heavier than an electron, the electrons respond more rapidly to surrounding changes than nuclei. Thus Schrödinger equation solution for nuclei and electrons can be separated into separate mathematical problems and this is termed as the Born-Oppenheimer approximation. Based on this approximation, the Hamiltonian operator of time-independent Schrödinger equation can be expanded as described in Equation 1-2.
\[
\left[-\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla^2_i + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r_i, r_j) \right] \Psi = E \Psi
\] (1-2)

Here, the first term of the Hamiltonian operator describes kinetic energy of each electron with mass \(m_e\), the second term describes interaction energy between each electron and the collection of atomic nuclei and the final term in the operator represents interaction energy between different electrons. \(E\) is the ground state energy of the system which is the lowest energy associated with an arrangement of electrons in the field of a set of nuclei. The electronic wave function \(\Psi\) is a function of spatial coordinates of each of the \(N\) electrons and can be approximated as the product of individual electron wave functions which is termed as Hartee product \(\Psi = \Psi_1(r), ..., \Psi_N(r)\). The product of wave functions \(n(r) = 2 \sum_i \Psi_i^*(r)\Psi_i(r)\) is the probability that an electron in individual wave function is located at position \(r\).

The Schrodinger equation is a many-body problem. It can be simplified by representing individual wave functions in terms of electron density \(n(r)\) which is a function of only three coordinates and contains significant physically observable information.

1.2.2 Kohn-Sham Equations

The building blocks of DFT are the two mathematical theorems proved by Kohn and Hohenberg and the set of equations derived by Kohn and Sham. The first theorem by Kohn and Hohenberg states the ground-state energy determined from Schrodinger's equation to be a unique functional of the electron density. The second theorem is referred to as the variational principle and it states the electron density that minimizes the energy of the overall functional to be the true electron density.
corresponding to the full solution of the Schrödinger equation. Note that the functional is described in terms of single-electron wave functions \( \Psi_i(r) \) which collectively define electron density \( n(r) \) and hence there is a one-to-one mapping between the ground-state wave function and the ground-state electron density. The energy functional can be written as a sum of \( E_{\text{known}}[\{\Psi_i\}] \) and \( E_{\text{XC}}[\{\Psi_i\}] \). \( E_{\text{known}}[\{\Psi_i\}] \) describes electron kinetic energies, Coulomb interactions between electrons and nuclei, Coulomb interaction between pairs of electrons and Coulomb interaction between pairs of nuclei while \( E_{\text{XC}}[\{\Psi_i\}] \) is the exchange-correlation functional and accounts for all the quantum mechanical effects that are not included in the “known” terms.

Kohn and Sham demonstrated that the correct electron density can be determined by solving a set of equations where each equation considers interactions of a single electron. The Kohn-Sham equations are written as

\[
\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V(r) + V_H(r) + V_{\text{XC}}(r) \right] \Psi_i(r) = \varepsilon_i \Psi_i(r)
\]  

(1-3)

where, \( V \) is the known part of the total functional that describes the interaction between an electron and the collection of nuclei, \( V_H \) also termed as the Hartree potential describes Coulomb repulsion between the specific electron and total electron density and \( V_{\text{XC}} \) describes exchange and correlation contributions to the single electron equations and is a functional derivative of the exchange-correlation energy.

In order to solve Kohn-Sham equations, the potential terms need to be determined and they can be described in terms of electron density. To find electron density, the single-electron wave functions is to be known for which solution of Kohn-Sham equation is required. Hence an iterative algorithm is employed to solve this
closed loop problem which is also referred to as electronic relaxation or self-consistent field (SCF) calculation. Figure 1-1 describes the functioning of DFT. Orange box highlights the steps involved in electronic relaxation while the blue box describes ionic or geometric relaxation. Based on supplied arrangement of atoms, an initial trial electron density is defined for the electronic relaxation. Employing this trial electron density, Kohn-Sham equation is solved for the single particle wave function ($\psi_i$) from which the Kohn-Sham electron density ($n_{KS}(r)$) is determined. Now, energy of Kohn-Sham electron density is compared with that of the initial trial electron density. If the energies are equal or the difference within a set parameter, calculation is said to have attained self-consistency and based on variational principle, this electron density corresponds to the ground-state density for the supplied structure of atoms. However, if the energies are considerably different, a new trial electron density is defined and the electronic loop is repeated till self-consistency is attained. Once a calculation is self-consistent, using energies of the ground state electron density, the inter-atomic forces are tested for force convergence criterion. If the criterion is not met, based on calculated forces, the atoms are rearranged and electronic relaxations followed by force analysis are performed on this new configuration. This combination of electronic and ionic relaxations is performed till the configuration corresponds to a critical point (relaxed structure). Note that the determined critical point could be a saddle point and not a true minima. Normal mode analysis enables identifying saddle points and is described in subsequent sections. Energies of multiple minima are compared to identify the global minimum.
1.2.3 Exchange-Correlation Functionals

In the treatment of electrons as point particles, change in position of one point particle influences a second particle due to inter-particle interaction. However in the case of electron densities, one electron density does not directly influence another density. The exchange-correlation is a potential that corrects for two components. The exchange portion accounts for the energy change of the total system if two electrons with different coordinates are interchanged while the correlation portion considers a collection of electrons as no longer point particles but as electronic densities. In order to solve Kohn-Sham equations, the exchange-correlation function ($E_{XC}[[\Psi_i]]$) is to be known. Exact form of this functional will account for all quantum-mechanical effects and yield the true solution. However, exact form of the exchange-correlation functional is still unknown even though its existence is guaranteed by the Kohn and Hohenberg theorems.
Various approximations of the exchange-correlation functional have been developed to determine an approximate solution to Kohn-Sham equation. In local density approximation (LDA), exchange-correlation potential for an electron density is set equal to the known exchange-correlation potential of a homogenous electron gas with the same density. It is represented in Equation 1-4.

\[ V_{XC}(r) = V_{XC}^{\text{electron gas}}[n(r)] \quad (1-4) \]

LDA is only suitable for systems with slow uniform variation of electron densities such as bulk metals and is of limited value in materials with interfaces where due to chemical bonds, there are significant variations in electron density. Even though LDA agrees with experiments for structural and vibrational data, it overestimates bond energies and consequently bond lengths.

In generalized gradient approximation (GGA), local gradient in the electron density is considered alongside local electron density as shown in Equation 1-5

\[ V_{XC}(r) = V_{XC}^{\text{electron gas}}[n(r), \nabla n(r)] \quad (1-5) \]

where, \( \nabla n(r) \) is the gradient of the electron density. GGA is more accurate than LDA especially in describing systems with sharper variation in electron density such as surfaces and small molecules. However GGA is observed to slightly underestimate bond energies and thus resulting in slight overestimation of lattice constants. Since the gradient in GGA can be treated differently, there are a few distinct GGA functionals. Notable among these are Perdew-Wang 1991 (PW91)\(^{32}\) and Perdew-Burke-Ernzerhof (PBE)\(^{33}\) functionals. Studies presented in this report employ the PBE functional.
Beside LDA and GGA there are newer functionals that include more physics such as meta-GGA which also considers $V^2 n(r)$ (Tao-Perdew-Staroverov-Scuseria (TPSS))\textsuperscript{34} and hyper-GGA or hybrid functionals that combine different proportions of LDA and GGA (Becke-Lee-Yang-Parr (B3LYP))\textsuperscript{35,36} or combine different proportions of PBE functionals along with Hartree-Fock exchange (Heyd-Scuseria-Ernzerhof (HSE))\textsuperscript{37}. Though these hybrid functionals are more accurate, they come along with significant increases in computational cost.

1.2.4 Pseudopotentials

The electronic wave functions can be expanded through the use of a series of plane waves. However, in order to represent all of the electrons associated with a particular atom, very large plane wave sets would be required. Note that core electrons are not generally important in chemical bonding or defining material properties. Pseudo potential is an effective potential that replaces the atomic all-electron potential such that core electrons are eliminated while the valence electrons are described by nodeless pseudo-wave function. Electron density of the core electrons is replaced with a smoothed density that approximates the properties of the true ionic core which if fixed is referred to as the frozen core model or else as all-electron calculation. Calculations based on frozen core model are more common than all-electron calculations. Norm-conserving pseudo potentials are derived from an atomic reference state and enforce the condition that outside a cutoff radius, the norm of each pseudo wave function is identical to its corresponding all-electron wave function. Ultra soft pseudo potentials (USPP)\textsuperscript{38} relax the norm-conserving constraint to further reduce the basis set size. Projector augmented wave (PAW)\textsuperscript{39} pseudo potential transforms the rapidly oscillating
valence wave functions near the ion cores into smooth wave functions and improves computational convenience since rapid oscillations would require many Fourier components to accurately describe the wave function. Though USPP and PAW give similar results in most systems, for systems with large difference in electronegativity or strong magnetic moments, the PAW pseudo potentials are preferred.

1.3 Dispersion-Corrected Density Functional Theory

Though DFT is a powerful computational tool, it has certain limitations such as inability to describe electron distribution in systems with excited states, failure to accurately predict band gap of insulators and semi-conductors and its incapability to account for van der Waals (vdW)/dispersion interactions.\(^{40}\) Inclusion of vdW interactions is observed to be imperative for the systems studied in this report. van der Waals interactions comprise of Debye forces existing between a permanent dipole and London dispersion forces that exists between two instantaneously induced dipoles. These forces are seen to exist even in neutral systems\(^{41}\) where due to no electron density overlap, prevents DFT from being able to capture the physics. Incorporating dispersion into DFT is a field of active research with different techniques to address the issue.\(^{42-47}\) Based on the treatment of dispersion in DFT, these techniques can be classified as implicit electronic treatment or explicit electronic treatment. Implicit treatment involves modifying/developing exchange-correlation functionals that account for dispersion within the electronic relaxation.

\[
E_{XC}(r) = E_{XC}^{LDA}(r) + E_{XC}^{nl}(r) \tag{1-6}
\]

The non-linear exchange \((E_{XC}^{nl}(r))\) accounts for the longest ranged or most non local terms and describes vdW interaction. In certain systems where dative bonding is well
described by conventional exchange-correlation functionals, implicit treatment is observed to overestimate the binding energies.\textsuperscript{48} This is due to the need for parameterization of $E_{xc}^{nl}$ based on the structure of system being studied and hence the developed functional is not transferrable. Explicit treatment involves evaluating dispersion effects ($E_{vdW}, F_{vdW}$) separately and adding the forces and energies to that determined by conventional electronic relaxation ($E_{DFT}, F_{DFT}$). These total energies and forces ($E_{DFT+D}, F_{DFT+D}$) are considered for the ionic relaxation.

\[ E_{DFT+D} = E_{DFT} + E_{vdW}; F_{DFT+D} = F_{DFT} + F_{vdW} \]  \hfill (1-7)

1.4 L(S)DA+U and Hybrid Functionals

Though L(S-spin)DA has been very successful in describing systems with delocalized electrons, it fails to describe systems with strongly correlated $d$ and $f$ electrons. This is because L(S)DA does not take into account the on-site Coulomb interaction. L(S)DA tends to delocalize electrons over the system and each electron feels an average of the Coulombic potential. Furthermore, treatment of exchange-correlation potential as a spherical, orbital-independent potential results in the inability to give a correct band gap for semiconductors and insulators. This limitation of L(S)DA can be remedied by addition of a Hubbard-like localized term to the L(S)DA functional and the approach is referred to as L(S)DA+U or (DFT+U). In the actual approach, localized $d$ and $f$ electrons are separated from delocalized $s$ and $p$ electrons and the latter is correctly described by normal LDA while the Hubbard term (defined by a U parameter) acts on the former. In order to avoid double counting of the correlation part for localized electrons, a term called the double counting correction (defined by a J parameter) is subtracted from the Hamiltonian. The ‘U’ and ‘J’ parameters represent
intra-atomic Coulomb and exchange terms respectively. Based on the evaluation of double counting correction and treatment of ‘U’ and ‘J’ parameters, there are two prominent L(S)DA+U techniques developed by Liechtenstein et al and Dudarev et al.\textsuperscript{49}.\textsuperscript{50} ‘U’ and ‘J’ parameters are initially set such that certain computed properties of the system such as band gap or energy match values determined experimentally or by higher functionals.

Hybrid functionals are a class of approximations to the exchange-correlation energy functional where a portion of exact exchange from Hartree-Fock is incorporated with exchange and correlation from other sources. The hybridization technique provides a simple scheme for improving many molecular properties such as bond lengths, vibration frequencies and atomization energies. Hybrid exchange-correlation functional is usually constructed as a linear combination of Hartree-Fock exact exchange functional ($E^{\text{HF}}_x$) and any number of exchange and correlation explicit density functionals. The parameters determining weight of each functional is evaluated by fitting the functional’s prediction to experimental data. The B3LYP exchange-correlation functional is determined as

$$E_{xc}^{\text{B3LYP}} = E_{xc}^{\text{LDA}} + a_o(E^{\text{HF}}_x - E_{xc}^{\text{LDA}}) + a_x(E^{\text{GGA}}_x - E_{xc}^{\text{LDA}}) + a_c(E^{\text{GGA}}_c - E_{xc}^{\text{LDA}})$$ \hspace{1cm} (1-8)\textsuperscript{a}

where, $a_o = 0.2$, $a_x = 0.72$ and $a_c = 0.81$. HSE functional separates exchange energy into short range (SR) and long range (LR) where, the short range exchange is mixed with a non-local Hartree-Fock exchange by a certain fraction while the long range exchange comes from PBE semi-local approximation. HSE exchange-correlation functional uses an error function screened Coulomb potential to calculate the exchange portion of the energy in order to improve computational efficiency and is determined as
\[ E_{xc}^{PBEh} = aE_x^{HF,SR}(\omega) + (1 - a)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE} \]  

(1-9)

where, \( a \) is the mixing parameter for the Fock exchange and \( \omega \) is an adjustable parameter controlling the range of electron interaction. The mixing of Fock exchange is motivated from Coulomb-hole-plus-screened exchange (COHSEX) approximation for quasiparticle theory and Thomas-Fermi model of screening. When \( \omega = 0 \), the HSE functional becomes PBE0 hybrid functional.

1.5 Analytical Methods

1.5.1 Normal Mode Analysis

Molecular vibrations result from the periodic motions of atoms in a molecule while the molecule as a whole has a constant translational and rotational motion. Each of this periodic motion is referred to as a vibration mode or state and the corresponding frequency is termed as vibrational frequency. An isolated non-linear molecule with \( N \) atoms has \( 3N - 6 \) modes of vibration where the 6 modes correspond to free motions associated with translation and rotation about \( x, y \) and \( z \) axis. A linear molecule has \( 3N - 5 \) modes while a diatomic molecule has only one mode of vibration. When a molecule chemisorbs on a surface, the 6 modes corresponding to free rotation and translation are hindered by the surface and become non-redundant. Experimentally, the vibrational states can be probed employing infrared spectroscopy or Raman spectroscopy. In DFT, vibrational states can be determined from the dynamical matrix evaluated by numerical finite difference method.\(^{51, 52}\) The rows of the dynamical matrix are evaluated from atomic forces obtained when atoms are displaced from their equilibrium position by a small shift and the energy is iteratively minimized again. Subsequent diagonalization of the dynamical matrix yields frequency and eigenvectors of the normal mode of
vibrations. Vibrational modes are used to understand the mode softening (red-phase shift) of a chemisorbing molecule, to apply zero-point corrections and to identify critical points (relaxed structure) predicted by DFT as true minima or saddle points.

1.5.2 Charge Density Analysis

As discussed previously, DFT through a combination of electronic and ionic relaxations, determines the ground state electron density of a molecular system being investigated. This electron density can be decomposed to determine charges on individual atoms. Charge analysis provides information on the type of bonding adopted by molecular species on a surface and identifies charge redistribution during chemisorptions and reaction processes. Insight of charge redistribution helps in identifying bond cleavages to be homolytic or heterolytic and polarization effects on the surface. Bader analysis and density derived electron charge (DDEC) analysis are two prominent charge analysis techniques.

1.5.2.1 Bader

Richard Bader developed a concept titled ‘Quantum Theory of Atoms in Molecules’ where he presented an intuitive technique to spatially divide a molecule into atoms. The idea was to use charge density to divide space within molecular systems into atomic (Bader) volumes. Atoms are divided into Bader volumes using a zero-flux surface which is a 2-dimensional surface on which the charge density is a minimum perpendicular to the surface. In molecular systems, the charge density is maximum at each atomic center and reaches a minimum between atoms. This is where the atoms can be separated from each other. There are several different approaches (algorithms) to determine the zero-flux surface. Early algorithms calculated the gradient of the charge density from derivatives of an analytic wavefunction where stationary points
in the charge density are determined and trajectories along the density gradient from these points are followed to map out their connectivity and the zero-flux dividing surface. These techniques are apt for small molecules while are criticized as being computationally expensive in large systems. Henkelman et al,56 presented a novel technique where trajectories are constrained to grid points at which charge density gradients are evaluated and a correction vector is calculated which points from the nearest grid point to the unbiased (off-lattice) trajectory. This algorithm allows convergence in the limit of a fine charge density grid and is suitable for large DFT calculations.

1.5.2.2 Density derived Electrostatic and Chemical Charge Analysis

Assigning net atomic charges to individual atoms from electron densities obtained from quantum chemistry calculations is challenging. Widely applicable approach should satisfy several criteria such as applicability to both periodic and non-periodic systems, accurate reproducibility of electrostatic potential outside the electron distribution, assigned atomic distributions should resemble those of real atoms in appropriate reference states and the atomic charges should be independent of the basis sets used to generate electron density. Bader net atomic charges are chemically meaningful but they do not accurately reproduce electrostatic potential outside the electron distribution. Density derived electrostatic and chemical (DDEC) charge analysis57 optimizes the net atomic charges to be chemically meaningful. It accurately reproduces electrostatic potential outside the electron distribution by simultaneously optimizing atomic electron density distributions to be close to spherically symmetric and to resemble reference state atoms. The DDEC method accounts for charge transfer that
takes place in materials involving ionic bonding, covalent bonding, charge compensation and dielectric screening.

1.5.3 Projection of Density of States onto Bader Regions

Density of states (DOS) is a description of the number of electronic states at each energy level available to be occupied by electrons. High density at specific energy levels translates to the availability of many states for occupation while a DOS of zero indicates that no states can be occupied at that energy level. DOS analysis provides an insight into the electronic band structure of a system and helps identify valence and conduction bands, band gaps and Fermi-level of a system. Valence band is the highest range of electron energies in which electrons are present when the system is at absolute zero temperature. Valence band is located below the conduction band which is the range of electron energies enough to free an electron from its binding with an atom and move freely within the atomic lattice of the material as a delocalized electron. Separation between valence and conduction band is referred to as the band gap and no electron states exist in this region. The Fermi-level is a hypothetical energy level that represents the total chemical potential for electrons in a system.

Local density of states (LDOS) describes space-resolved density of states. The DOS can be calculated using wave functions in DFT. To calculate LDOS, the charge density of each electronic eigenstate is projected onto Bader regions. DFT provides both site and angular momentum projected DOS, which allows to examine the DOS projected onto molecular orbitals of each individual atom in the system. The projected density of states (pDOS) is useful in analyzing chemical bonding of an adsorbate to a substrate. In order to analyze pDOS for a specific atom on a surface, based on type of complex (square planar, octahedral, etc) formed by the atom, the supercell needs to be
rotated such that $x$, $y$ and $z$ axis align along the corresponding $p$ or $d$ orbital interactions with the neighboring atoms. This ensures accurate projection of the molecular orbitals onto the Bader regions.

### 1.5.4 Nudged Elastic Band Method

Nudged elastic band method (NEB)\textsuperscript{59} is a computational technique widely used in the fields of theoretical chemistry, physics and material science, to determine saddle points and minimum energy pathway (MEP) between a pair of stable states. The method involves determining the lowest possible energy (optimizing) for a number of intermediate images along the reaction pathway while maintaining equal spacing between neighboring images. It utilizes the property of a MEP that any point on the path is at an energy minimum in all direction perpendicular to the path. The constrained optimization of images along the NEB is done by adding spring forces along the band between images while projecting force component due to the potential on to the band.

The climbing image NEB method\textsuperscript{60} is a slight modification of regular NEB and involves a rigorous convergence to a saddle point and hence determines the transition state for a MEP. In the climbing image NEB, after a few iterations with regular NEB, the image with the highest energy is identified and is referred to as the climbing image. This image does not feel the spring forces and tries to maximize it’s energy along the band while minimizing in all other directions. As the image moves up the potential energy surface along the elastic band and down the surface perpendicular to the band, other images in the band serve the purpose of defining the one degree of freedom for which a maximization of the energy is carried out. Note that as the climbing image moves up the saddle point, images on one side will get compressed while that on the
other side will spread out. Upon convergence, the climbing image is a guaranteed saddle point but is still confirmed to be a transition state through normal mode analysis examining for an imaginary mode.
CHAPTER 2
PRECURSOR-MEDIATED DISSOCIATION OF \textit{n}-BUTANE ON A PdO(101) THIN FILM

2.1 Motivation

Alkane activation by transition metals has attracted significant interest due to the desire to more effectively utilize alkanes in power generation applications and to develop improved strategies for transforming alkanes to chemicals of greater value. Indeed, developing catalysts that can efficiently convert methane to higher alkanes or organic oxygenates could have a profound impact on the commercial utilization of natural gas. The adsorption of alkanes on solid surfaces has been investigated extensively, with most studies focusing on clean transition-metal (TM) surfaces. While this prior work has greatly advanced the fundamental understanding of alkane activation on metallic surfaces, there is a significant need to characterize the elementary interactions between alkanes and TM oxide surfaces as well. A key reason is that several applications of oxidation catalysis occur under conditions that cause TM surfaces to oxidize, often resulting in dramatic changes in catalytic properties.

Of particular relevance to the present study is the catalytic combustion of CH\textsubscript{4} in lean gas turbines. Prior studies show that Pd catalysts perform exceptionally well in this application because the catalysts oxidize to a PdO phase which has a high activity for methane oxidation.\textsuperscript{4, 5, 9, 62-70} These findings certainly provide strong motivation for investigating the surface chemistry of PdO in detail. In this chapter, the adsorption and oxidation of \textit{n}-butane on a PdO(101) thin film is investigated focusing particularly on the role of adsorbed $\sigma$-complexes as precursors for initial C-H bond activation.

Previous investigations show that the initial dissociation of alkanes on transition metal surfaces can occur by two general mechanisms, namely, a direct mechanism and a precursor-mediated mechanism. In the direct mechanism, the alkane molecules dissociate in a single gas-surface collision without thermally accommodating to the surface. The probability for direct dissociation generally increases with increasing gas kinetic energy since energetic molecules can more readily surmount activation barriers for dissociation during a single collision. The precursor-mediated mechanism is fundamentally different from the direct mechanism. In the precursor-mediated mechanism, alkanes first adsorb into a molecular state and then dissociate. In this process, the molecularly adsorbed species act as a precursor to dissociation and a kinetic competition between desorption and dissociation determines the net probability for dissociation. Since the molecular adsorption of alkanes is non-activated, precursor-mediated dissociation becomes increasingly more probable as the gas kinetic energy decreases and should thus be dominant under typical reaction conditions.

Key characteristics of alkane dissociation by the precursor-mediated mechanism are known from investigations with metal surfaces. Compared with a single gas-surface collision, adsorbing into the molecular state affords an alkane with a greater opportunity to explore the reactive potential energy surface and dissociate by a low energy pathway(s). However, since the alkane molecule dissipates its energy during adsorption, dissociation by the precursor-mediated mechanism requires the existence of low energy pathways for C-H bond cleavage. While the dissociative chemisorption of alkanes is typically activated with respect to the gas-phase zero, facile dissociation has been reported for a few metal surfaces, including the reconstructed Ir(110)\textsuperscript{71-74} and
Pt(110)\textsuperscript{75} surfaces and also at defect sites of Ir(111)\textsuperscript{76} and Pt(111).\textsuperscript{77} Dissociation is termed as facile for these systems because the activation energies for dissociation are lower than those for desorption. A trend that emerges from these prior studies is that low-coordination sites on metallic Pt and Ir surfaces are more reactive than close-packed terraces toward the activation of molecularly adsorbed alkanes. This higher reactivity appears to be a consequence of lower energy barriers for C-H bond cleavage, rather than resulting from longer lifetimes of alkane molecules at the low-coordination sites. An interesting possibility is that alkane dissociation barriers are strongly dependent on the local coordinative environment on non-metallic surfaces as well. Establishing such a relationship could aid in advancing a more general understanding of the factors which facilitate alkane activation.

Experimental UHV studies have found that propane undergoes facile C-H bond cleavage on the PdO(101) surface, with dissociation occurring below 200 K.\textsuperscript{78} The initial C-H bond cleavage occurs by a precursor-mediated mechanism in which a strongly-bound molecular state serves as the precursor to dissociation. Using temperature programmed desorption (TPD) and density functional theory (DFT) calculations, it is shown that small alkanes bind strongly on PdO(101) by forming $\sigma$-complexes on coordinatively unsaturated (\textit{cus}) Pd atoms of the surface.\textsuperscript{79} The bonding of the alkane $\sigma$-complexes is analogous to that in organometallic complexes\textsuperscript{80-82} and involves both electron donation and back-donation from/to the alkane molecule and Pd $d$-states. In addition to enhancing the alkane binding strengths on PdO(101), $\sigma$-complex formation also weakens the coordinated C-H bonds as evidenced by bond elongation and softening of vibrational modes.\textsuperscript{79} Thus, the formation of strongly-bound alkane $\sigma$-
complexes on PdO(101) appears to electronically activate C-H bonds in addition to prolonging the surface lifetimes of the molecular precursors. Studies have also shown that H₂ also forms a σ-complex on PdO(101) that acts as precursor to dissociation.⁸³

Taken together, these results point toward a general role of adsorbed σ-complexes as precursors in the activation of saturated molecules on PdO(101) and possibly other late TM oxides. The ability of the cus-Pd sites of PdO(101) to activate alkane C-H bonds bears a striking similarity to the high reactivity of under-coordinated sites of metallic surfaces reported in early studies of alkane activation.⁶¹

In this chapter, adsorption and activation of n-butane on PdO(101) is investigated along with the properties of adsorbed alkane σ-complexes and their role as precursors for C-H bond activation on PdO(101). Similar to the smaller alkanes, n-butane forms relatively strongly-bound σ-complexes on PdO(101), and these species serve as the precursors for initial C-H bond cleavage. DFT calculations reveal that coordination to cus-Pd atoms on PdO(101) electronically activates C-H bonds of adsorbed alkane σ-complexes, thereby lowering energy barriers for C-H bond cleavage.

2.2 Computational Details

All the DFT calculations for this study were performed using the Vienna ab initio simulation package (VASP).⁸⁴-⁸⁷ The calculation details are similar to those used in earlier studies by Weaver et al on the adsorption of H₂O, H₂, and alkanes on PdO(101).⁷⁹, ⁸³, ⁸⁸ The projector augmented wave (PAW)³⁹, ⁸⁹ pseudo potentials provided in the VASP database is used. Calculations have been done using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.³³ An experimental band gap of ~ 1 eV has been reported for polycrystalline PdO⁹⁰ but standard GGA-DFT shows no band gap.
The effects of using GGA+U to correct for the band gap have been previously tested and while the adsorption energies are modified, the general conclusions about the relative stability of species on the surface are not affected. Furthermore, earlier studies of adsorbed H$_2$O, H$_2$, and alkanes show better quantitative agreement between TPD-derived adsorption energies and barriers of elementary processes (e.g. H$_2$O and H$_2$ dissociation and association) and GGA-DFT values without the +U implementation. Since the primary interest is in determining the adsorption energies and surface reaction barriers, all calculations are done with standard GGA-DFT. A plane wave expansion with a cutoff of 400 eV is used and the total energy calculations are done using the conjugate-gradient method for electronic relaxations, accelerated using Fermi-level smearing with a Gaussian width of 0.1 eV. In an earlier study to determine relevant minima for the alkane configurations on PdO(101), the positions of atoms are relaxed until the forces on all unconstrained atoms are less than 0.03 eV/Å. For the study presented in this chapter, the force criterion has been further refined to 0.01 eV/Å. This stricter criterion is important in accurately evaluating the very low frequency modes (~50 cm$^{-1}$) of alkanes on the surface. These modes involve mainly rotation of the molecule on top of cus-Pd sites, and without proper accuracy of the forces, these low frequency modes appear as an imaginary mode in the normal mode calculations because of the flat potential energy surface along that particular mode. The stricter force criterion changes the adsorption energy of the alkanes by about 1 kJ/mol. Several minima with $\eta^1$(H,H) interactions with cus-Pd atoms that lie within this range were identified, and there is some crossover in the favored configurations after relaxing to 0.01 eV/Å but these changes are minor and do not affect the conclusions of the study. The only
minimum that shows a more noticeable difference in the nature of the bonding is the favored \( r^2 \) propane configuration, which will be elaborated upon in subsequent sections. In considering the adsorption energies reported, it is important to note that DFT calculations do not capture dispersion interactions. However, dispersion-corrected DFT calculations are presented in the subsequent chapters. Inclusion of dispersion interactions is seen to improve binding energy predictions of alkane on PdO(101), but since these interactions are lesser sensitive than dative interactions, only minor geometric differences in predicted configurations are observed.

The computational model of the PdO(101) film is represented with four layers (see Figure 2-1), which corresponds to a thickness of approximately 9 Å. The bottom layer is fixed but all other atoms in the oxide film and the adsorbates are allowed to relax. A vacuum spacing of 20 Å is maintained normal to the surface to minimize any spurious periodic interactions in this direction. The PdO(101) film is obtained from the relaxed PdO bulk structure \((a = 3.103 \, \text{Å}, \, c = 5.440 \, \text{Å})\), but the film is strained \((a = 3.057 \, \text{Å}, \, b = 6.352 \, \text{Å})\) to match the reported experimental structure.\(^{19}\) While experimentally the PdO(101) film is grown on Pd(111) surface, the oxide film is sufficiently thick (13 Å) that the Pd(111) substrate is ignored in DFT calculations. Inclusion of the Pd(111) substrate would require large supercells due to the lattice mismatch between the oxide film and the Pd(111) surface. A 1 \( \times \) 4 \((2 \times 2)\) surface supercell is used for alkanes adsorbed parallel (perpendicular) to the Pd \textit{cus} rows. Choice of the lateral dimensions ensures that the adsorbed alkane has negligible intermolecular interactions with periodic images. A \( k \)-point mesh of 4 \( \times \) 2 \( \times \) 1 \((2 \times 4 \times 1)\) is used for the 1 \( \times \) 4 \((2 \times 2)\) surface supercell.
Separate tests with additional slab thickness and finer \( k \)-point meshes reveal that they do not impact the results of the calculations.

![Figure 2-1](image)

Figure 2-1. Top and side view of the PdO(101) thin film structure. The orange and blue atoms represent O and Pd atoms, respectively. Rows of threefold-coordinated (\( cus \)) Pd and O atoms are indicated. The \( \bar{a} \) and \( \bar{b} \) directions correspond to the [010] and [101] crystallographic directions of PdO.

To find minimum energy pathways (MEP) and identify transition states (TS) for C-H cleavage for methane on the PdO(101) surface, the climbing nudged elastic band (NEB) method is used. Normal mode analysis is performed of the TS to ensure that only one imaginary mode exists. The vibrational modes are obtained by fixing the substrate and allowing only motion of the alkane molecule. The finite difference method implemented within VASP is used to determine the Hessian and vibrational modes. Displacements of 0.02 Å were found to be optimal to ensure that very low frequency modes (~50 cm\(^{-1}\)) found for alkanes adsorbed on the surface were accurately...
evaluated. Normal-mode calculation tests of adsorbed methane that includes the motion of \textit{cus}-Pd atoms involved in the bonding were also performed and differences of only 5 cm\textsuperscript{-1} in the vibrational frequencies were observed. These differences are not significant to influence the conclusions made in this chapter.

\section*{2.3 Results and Discussion}

\subsection*{2.3.1 Experimental Observations}

Temperature programmed reaction spectroscopy (TPRS) and temperature programmed desorption (TPD) experiments were performed to study chemisorption and activity of \textit{n}-butane on PdO(101). TPRS spectra illustrated the evolution of both CO\textsubscript{2} and H\textsubscript{2}O which demonstrates the PdO(101) surface is active for the complete oxidation of \textit{n}-butane. CO\textsubscript{2} is observed to desorb predominantly in a single peak at about 475 K while H\textsubscript{2}O desorption traces exhibits a small peak at 337 K as well as a more intense feature at about 475 K. Based on prior investigations of H\textsubscript{2} and H\textsubscript{2}O adsorption on PdO(101), the H\textsubscript{2}O TPD peak at 337 K is attributed to desorption-limited water\textsuperscript{83, 88} while the concurrent desorption of H\textsubscript{2}O and CO\textsubscript{2} at 475 K is characteristic of the reaction-limited oxidation of hydrocarbon fragments. Overall, the TPRS results demonstrate that a fraction of \textit{n}-butane molecules exposed to PdO(101) undergo dissociative chemisorption, and that the resulting fragments are completely oxidized by the surface at about 450 K. Considering prior studies of alkane adsorption\textsuperscript{61} the initial activation of \textit{n}-butane on PdO(101) is expected to occur by cleavage of a single C-H bond.

An insight of \textit{n}-butane bonding on Pd(111) and PdO(101) can be obtained by comparing TPD spectra of the alkane on these surfaces. A single distinct desorption peak is observed for butane on Pd(111) while the traces obtained from PdO(101) are
very broad, and exhibit several distinct peaks. This can be interpreted as the \( n \)-butane molecules encountering a wider range of binding environments on PdO(101) compared to Pd(111). This diversity is likely due to the structural and compositional heterogeneity of the oxide surface. The higher temperature peak referred to as \( \alpha_1 \) corresponds to the strongly-bound states, and with increase in coverages they tend to populate initially followed by the weaker bound states. On PdO(101) the \( \alpha_1 \) peak of \( n \)-butane is centered at about 220 K while on Pd(111) it is at about 195 K. The higher temperature peak of \( n \)-butane on PdO(101) compared to Pd(111) supports the formation of \( n \)-butane \( \sigma \)-complex(s) on PdO(101). Analysis of the TPD data shows that the binding energy of \( n \)-butane \( \sigma \)-complex closely follows the energy versus chain length (\( E \) vs. \( N \)) trend that was reported for \( \sigma \)-complexes of smaller alkanes on PdO(101) (Figure 2-2).

The non-zero energy intercept for PdO(101) was attributed to a nearly constant contribution made by \( \sigma \)-complex formation, thus interpreting that that the molecule-surface dispersion interaction is the dominant cause of the linear increase in binding energy with increasing chain length of alkanes adsorbed on the oxide. The observation is also intriguing since one would expect that increasing the chain length would allow alkanes to form multiple dative bonds with the PdO surface and thereby experience a greater enhancement in binding on PdO(101) versus Pd(111) compared with smaller alkanes. While this possibility certainly exists, \( n \)-butane does not appear to be long enough to experience such additional enhancements in binding on PdO(101). The DFT results presented in subsequent sections are seen to support this interpretation.

The evolution of product yields with the \( n \)-butane exposure provides evidence that the \( \alpha_1 \) state serves as the precursor to the initial C-H bond cleavage of \( n \)-butane on
PdO(101). This is similar to the behavior observed in the dissociation of propane on PdO(101)\textsuperscript{78} which suggests a more general conclusion that the formation of adsorbed $\sigma$-complexes is a necessary first step in the activation of alkanes on the PdO(101) surface.

Figure 2-2. Binding energy vs. chain length of linear C\textsubscript{1} to C\textsubscript{4} alkanes on Pd(111) and PdO(101). The desorption pre-factors for Pd(111) were taken from ref.93 and those for alkanes on PdO(101) represent maximum values determined from transition state theory.

Further characterization of $n$-butane $\sigma$-complex formation on PdO(101) was done by examining the influence of pre-adsorbed $^{18}$O\textsubscript{2}. Earlier TPD studies\textsuperscript{94} and DFT calculations predict that O\textsubscript{2} binds at \textit{cus}-Pd sites on PdO(101). Pre-adsorbing O\textsubscript{2} is observed to cause the $\alpha_1$ peak and CO\textsubscript{2} yield to decrease suggesting $n$-butane chemisorbs along the \textit{cus}-Pd row on PdO(101). However, smaller decrease in yield
compared to \( \alpha_1 \) desorbed yield indicates an increase in \( n \)-butane dissociation probability on \( O_2 \) pre-adsorbed PdO(101). Through experimental analysis, it is deduced that \(^{18}O_2\) molecules do not completely block \( n \)-butane adsorption on PdO(101) but rather shift the population of butane towards more weakly bound configurations.

### 2.3.2 Alkane \( \sigma \)-complexes

DFT is used to explore the bonding of \( n \)-butane \( \sigma \)-complexes on PdO(101), and to generally clarify how the nature of the alkane-Pd dative interaction influences C-H bond activation. In an earlier DFT study it was reported that alkanes coordinate with \( cus \)-Pd atom(s) to form adsorbed \( \sigma \)-complexes.\(^{79}\) Charge density difference plots of methane adsorbed on \( cus \)-Pd atoms clearly show the donation back-donation features, which is indicative of dative bonding. The adsorption energies from DFT, while not capturing the substantial dispersion interactions, show that alkane bonding on PdO(101) surface is much stronger than corresponding adsorption on Pd(111). The C-H bonds involved in the coordinate interaction(s) are stretched from their gas-phase values. Red-shifts in vibrational modes associated with these bonds were also observed. These effects suggest that the dative bonding weakens the coordinated C-H bonds, making them easier to cleave. This model of alkane bonding on the PdO(101) surface helps to explain the experimental observations of adsorbed \( \sigma \)-complexes of propane and \( n \)-butane serving as precursors to initial C-H bond cleavage.

In this chapter, DFT studies have been extended to the adsorption of \( n \)-butane on PdO(101). Earlier study identified multiple \( \eta^2 \) and \( \eta^1 \) configurations for methane, ethane, and propane on PdO(101).\(^{79}\) Here those relaxed configurations are used as guesses to generate viable initial \( n \)-butane configurations that are subsequently relaxed.
Figure 2-3 A) and B) show the most stable $\eta^1$ and $\eta^2$ configurations of $n$-butane identified using DFT. $n$-butane in the $\eta^1$(2H) configuration has two H atoms interacting with cus-Pd atoms on the surface, and is favored over the single $\eta^2$(H,H) four-center bonding configuration by nearly 20 kJ/mol.

Figure 2-3. The favored $n$-butane configurations on PdO(101). A) $\eta^1$(2H) configuration with $E_{ads} = 31.2$ kJ/mol. B) $\eta^2$(H,H) configurations with $E_{ads} = 12.3$ kJ/mol. The $\eta^1$(2H) configuration involves two $\eta^1$ bonding interactions, while the $\eta^2$ configuration results in one weakened $\eta^2$ interaction.

A similar preference for $\eta^1$(2H) versus a single $\eta^2$(H,H) interaction for propane is observed but with only a 3.3 kJ/mol difference.\textsuperscript{79} This smaller difference between the $\eta^1$ and $\eta^2$ configurations of propane arises because the propane molecule can adopt an $\eta^2$(H,H) configuration involving the secondary carbon atom. $\eta^2$(C,H) configuration of propane (Figure 2-4 D)) that is slightly favored by 1 kJ/mol over the $\eta^2$(H,H) configuration (shown in Chapter 3, Figure 3-4 C)) is also identified. In both of these configurations, the propane molecule avoids steric repulsion from the adjacent surface.
atoms, and can thus adopt an optimal geometry for the $\eta^2$ interaction. A similar $\eta^2$ configuration is not possible for $n$-butane since it would bring non-bonded methyl groups too close to the PdO(101) surface. These steric interactions originate from the strong corrugation of the surface perpendicular to the $cua$-Pd row and occur when the long-chain alkanes align in that direction.

A clearer picture of the sensitivity of the four-center $\eta^2$(H,H) interaction to small geometric perturbations can be observed by comparing similar $\eta^2$ configurations for methane, ethane, propane, and $n$-butane. Figure 2-4 A) to C) show the same $\eta^2$ configuration for methane, ethane, and propane as the one depicted for $n$-butane in Figure 2-3 B). The adsorption energies for these three configurations are 16.2, 21.9, and 13.9 kJ/mol, respectively. When going from methane to ethane, the $\eta^2$ configuration maintains the strong coordinate bond in addition to attractive non-bonded interactions between the methyl group and the $cua$-O atom, but the propane molecule experiences a sharp drop in adsorption energy. This sharp drop is maintained for the $n$-butane molecule, which has an adsorption energy of 12.3 kJ/mol. In summary, a comparison of the $\eta^2$ configurations involving the CH$_3$ group shows a sudden drop in adsorption energy from ethane to propane. A visual inspection of Figure 2-3 A) and B) does not show much difference in the molecule-surface interaction of the methyl group, so the origin of the sudden drop in adsorption energy is not obvious.

The distortion cost of the molecule adsorbed on the surface is determined. The distortion cost or energy can be obtained by evaluating the energy of the molecule in the adsorbed configuration with the surface removed ($E_{molec,ads}$) and subtracting it from the energy of the gas-phase molecule ($E_{molec,gas}$).
Figure 2-4. $\eta^2$ configurations of methane, ethane and propane on PdO(101). A) Methane $\eta^2$ configuration with adsorption energy of 16.6 kJ/mol. B) Ethane $\eta^2$ configuration with adsorption energy 22.7 kJ/mol. C) Propane $\eta^2$ configuration with adsorption energy 13.9 kJ/mol. D) Most favored $\eta^2$ configuration of propane with adsorption energy 25.7 kJ/mol.

By this definition, a more negative value would indicate a greater strain or distortion energy, suggesting that intra molecular interactions are affected by adsorption on the surface. The analysis shows that propane and $n$-butane have lower distortion energies than ethane, thus demonstrating that molecular strain due to the surface is not responsible for the unfavorability of the $\eta^2$ configuration for the longer chain alkanes.
To separate the \( \eta^2 \) bonding interactions from other contributions from adjacent methyl groups, the spectator methyl group of the adsorption configuration for propane shown in Figure 2-4 C) is replaced with an H atom. The molecule and surface were then fixed and only the new H atom was allowed to relax to obtain an optimal C-H bond length. This procedure results in an ethane molecule bound to the surface in precisely the same manner as the propane molecule. The adsorption energy for this new ethane configuration is 13.4 kJ/mol, which is very similar to the propane and \( n \)-butane adsorption energies. Therefore, the spectator methyl groups of propane and \( n \)-butane are repelled sufficiently by the surface to prevent these molecules from achieving optimal bonding in the \( \eta^2 \) configuration. A more detailed analysis of the interaction between methyl group and \textit{cus}-Pd for ethane and the modified ethane shows that the modified ethane has a 12° rotation around the axis running along the \textit{cus}-Pd rows. This rotation disrupts the sensitive four-center interaction of the \( \eta^2 \)(H,H) configuration, resulting in a weaker bond. As noted earlier, this rotation is forced on the propane and \( n \)-butane configurations shown in Figure 2-4 C) and Figure 2-3 B) by the surface corrugation perpendicular to the \textit{cus}-Pd row. For propane, this perturbed \( \eta^2 \) configuration can be avoided by moving the coordinate bond to the secondary carbon atom (see Figure 2-4 D)), which allows the molecule to sit on top of a \textit{cus}-Pd atom with the adjacent methyl groups pointing away from the surface. Such a configuration is not an option for \( n \)-butane since the additional methyl group would have to be oriented toward the surface. As noted above, both \( \eta^2 \)(H,H) and \( \eta^2 \)(C,H) configurations for propane with very similar adsorption energies were identified. These two configurations are related by a small rotation around the axis running normal to the \textit{cus}-Pd rows, which
is distinct from the unfavorable rotation around the axis running along the cus-Pd rows that disrupts the \( \eta^2 \) interaction for propane and butane in Figure 2-4 C) and Figure 2-3 B). \( n \)-butane cannot adopt either the \( \eta^2(\text{H,H}) \) or \( \eta^2(\text{C,H}) \) configuration because of the considerable steric interactions with PdO(101) surface, which forces the weak bonding observed in Figure 2-3 B).

The above analysis clearly reveals that the methyl \( \eta^2 \) configuration is highly sensitive to the local geometry since the configuration involves a four center interaction. This sensitivity prevents stable minima of \( \eta^2 \) configurations from forming along the cus-Pd rows. As seen in the \( \eta^2 \) configuration of methane (Figure 2-4 A)), the downward oriented H atoms lie in the direction of the cus-Pd rows. Rotating methane bound atop cus-Pd molecule such that the downward oriented H-atoms gets closer to the cus-Pd results in a relaxed \( \eta^1 \) configuration with only one H-Pd interaction. These results indicate that the \( \eta^2(\text{H,H}) \) bonding is also disrupted if the H atoms are brought close to the adjacent cus-O atoms, which leaves the configuration in Figure 2-4 A) as the only stable \( \eta^2 \) configuration for CH\(_4\). Clearly, longer-chain alkanes that lie along the cus-Pd row will also be unable to adopt such an \( \eta^2 \) configuration. To confirm this idea, initial \( \eta^2 \) configurations of ethane, propane, and \( n \)-butane lying parallel to the cus-Pd row were prepared, and, as expected, each of these configurations relaxes into \( \eta^1 \) configurations such as that shown in Figure 2-3 A). With alkanes able to form only one \( \eta^2 \) bond and this bonding being weaker for the larger alkanes, it is clear that the \( \eta^1 \) configurations along the cus-Pd row will be the overwhelmingly favored adsorbed state of \( n \)-butane and longer straight-chain alkanes.
Propane holds a unique position in the transition from $\eta^2$ to $\eta^1$ configurations because it can adopt an $\eta^2$ configuration on its secondary carbon, which results in $\eta^1$ and $\eta^2$ configurations that are very similar in energy (~3 kJ/mol). For $n$-butane and larger straight-chain alkanes, DFT suggests that the component of the adsorption energy due to dative bonding interactions will scale as the number of $\eta^1$ interactions formed. For propane and $n$-butane, only two $\eta^1$ bonds can form due to the registry of the molecule on the PdO(101) surface. For propane, both of these bonds form on the CH$_3$ groups, while $n$-butane has one bond at a CH$_3$ group and the other at a CH$_2$ group. The adsorption energies of propane and $n$-butane in the $\eta^1(2H)$ configuration are 27.7 and 31.2 kJ/mol, respectively. While these values may indicate subtle differences in the strengths of $\eta^1$ bonds involving primary versus secondary C-H bonds, the energy difference is slight and could arise solely from non-bonding interactions. Future studies with longer alkanes that form three or more bonds will help to clarify this issue. Calculations that explicitly include the molecule-surface dispersion interaction are also required to fully account for the non-bonding interactions.

The adsorption of $n$-pentane on the PdO(101) surface is examined, and it is found that the favored bonding geometry is the $\eta^1(3H)$ configuration shown in Figure 2-5. In this configuration, the $n$-pentane molecule forms three $\eta^1$ bonds, one at each primary carbon atom and one at the central CH$_2$ group. The binding energies of the $\eta^1$ configurations of $n$-pentane are ~40 kJ/mol. This value of the binding energy is close to 3/2 of the binding energy for the $\eta^1(2H)$ propane configuration, which matches the ratio of $\eta^1$ bonds.
Figure 2-5. Favored \( \eta^1(3H) \) configurations of \( n \)-pentane on PdO(101). A) Staggered configuration with adsorption energy of 41.2 kJ/mol. B) Flat-lying configuration with adsorption energy of 40.7 kJ/mol. Notice that there are three H-Pd interactions in both these configurations.

This result suggests that the constant offset found in the experimentally-determined \( E \) vs. \( N \) relationship for methane to \( n \)-butane (shown in Figure 2-2) should breakdown and exhibit an abrupt increase at \( n \)-pentane if each of the \( \eta^1 \) bond strengths is in fact similar. Subsequent \( n \)-alkanes might also show a stepwise behavior in the offset, depending on the registry between the \( n \)-alkanes and the \textit{cus}-Pd row.

As shown in Figure 2-5, the \( \eta^1 \) configurations have freedom to rotate toward the neighboring fourfold Pd facet, while preserving the coordinate H-Pd bonds with the \textit{cus}-Pd row. For example, the configurations shown in Figure 2-5 A) and B) are related by a rotation around an axis parallel to the \textit{cus}-Pd rows. Both of these configurations share the same coordinate bonding, differing only in their non-bonding interactions with the
surrounding atoms. The difference in the adsorption energy of these two configurations is 0.5 kJ/mol. While not shown, observed similar results for n-butane and can conclude that the \( \eta^1 \) configurations have more rotational freedom since the two center interaction (Pd-H) is not as restrictive as the four-center interaction of the \( \eta^2 \) configuration. The rotational freedom of the \( \eta^1 \) configurations may allow these alkane \( \sigma \)-complexes to maximize their dispersion interaction with the surface, while maintaining relatively strong dative bonding with the \( \text{cus} \)-Pd row. In effect, the \( n \)-alkane \( \sigma \)-complexes could adopt a flat-lying geometry relative to the local facet, and experience a linear increase in the strength of the dispersion interaction with increasing chain length. Thus, the experimentally-observed \( E \) vs. \( N \) relation (Figure 2-2) appears to be consistent with propane and \( n \)-butane adsorbing in the \( \eta^1 \) configuration. Additional work that accurately includes dispersion will be needed to test this idea.

In earlier study of alkane \( \sigma \)-complexes on PdO(101), lengthening (~1.55%) of the two C-H bonds of CH\(_4\) that coordinate with the \( \text{cus} \)-Pd atom was reported. Furthermore, vibrational modes involving the symmetric and asymmetric C-H stretch of the weakened C-H bonds red-shift from the corresponding gas-phase values by \(~200 \text{ cm}^{-1}\). The magnitude of these red-shifts is much larger than those observed for alkanes on metal surfaces,\(^95\) and can be attributed to the dative bonding interaction on PdO(101). Table 2-1 shows the C-H bond stretching and mode softening of the symmetric and asymmetric stretch frequencies for the relevant minima identified for the alkanes on PdO(101) along with the relevant H-Pd bond distances for atoms involved in the coordinate bonding.
Table 2-1. The C-H and Pd-H bond lengths along with the associated mode softening of the C-H stretch frequencies for the relevant minima for the alkanes from methane to \( n \)-butane. Similar values for \( n \)-pentane except for the mode softening are also included. The % stretch of the C-H bond length with respect to the gas-phase is provided in brackets. The primary (CH\(_3\)) and secondary (CH\(_2\)) groups on the alkane are distinguished.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>C-H stretch (Å) [%]</th>
<th>Pd-H (Å)</th>
<th>Mode Softening (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH(_3)</td>
<td>CH(_2)</td>
<td>CH(_3)</td>
</tr>
<tr>
<td>( \eta^2 ) methane</td>
<td>1.114</td>
<td>-</td>
<td>2.160</td>
</tr>
<tr>
<td>( \eta^2 ) ethane</td>
<td>1.118, 1.123</td>
<td>1.106, 1.146</td>
<td>2.186, 2.126</td>
</tr>
<tr>
<td>( \eta^2 ) propane</td>
<td>-</td>
<td>-</td>
<td>2.601, 1.937</td>
</tr>
<tr>
<td>( \eta^1 ) propane</td>
<td>1.128</td>
<td>-</td>
<td>2.008</td>
</tr>
<tr>
<td>( \eta^1 ) butane</td>
<td>1.127</td>
<td>1.138</td>
<td>2.030</td>
</tr>
<tr>
<td>( \eta^1 ) pentane</td>
<td>1.125, 1.122</td>
<td>1.138</td>
<td>2.017, 2.012</td>
</tr>
</tbody>
</table>

Methane also shows softening of a bending mode (not shown) but for the other alkanes the dramatic softening (> 50 cm\(^{-1}\)) is restricted to stretching frequencies dominated exclusively by the C-H bond interacting with the \( \text{cus} \)-Pd atoms. The values for methane, ethane, and propane are slightly different than the values reported in a previous study\(^{61}\), \(^{79}\) due to the use of a force criterion of 0.01 (0.03) eV/Å and atomic displacements for the normal mode calculations of 0.02 (0.05) Å in the present (earlier\(^{79}\)) study. These changes are found to be necessary to properly refine the low frequency modes involved in rotation of the molecule on the surface. The change in the values reported in Table 2-1 are all minor and do not affect the conclusions from earlier study, except for the identification of a new \( \eta^2(\text{C,H}) \) propane configuration. As noted above, this configuration is very close in energy to the \( \eta^2(\text{H,H}) \) propane configuration reported in an earlier study.\(^{79}\) The inclusion of dispersion may differentiate these two configurations, but with
current DFT values, both can be expected to be present and indistinguishable within TPD.

Small increases in the percentage of C-H bond stretching with increasing alkane chain-length, independent of the type of bonding (\(\eta^1\) vs. \(\eta^2\)) is predicted. Since hyperconjugation can stabilize the weakening of a C-H bond, an ethane \(\sigma\)-complex may experience slightly more elongation of the C-H bonds and shorter H-Pd bonds compared with methane. The DFT results confirm this expectation (Table 2-1). Also, the mode softening scales with the extent of C-H bond stretching and therefore is more pronounced for longer alkanes. The alkane chain-length dependence of C-H bond stretching should become negligible with larger alkanes, and in fact a very little difference in the C-H bond lengths between \(n\)-butane and \(n\)-pentane is seen. Because of lack of symmetry between the two downward oriented C-H bonds within the \(\eta^2(C,H)\) propane configuration, the mode softening is associated with only one of the C-H bonds and is quite large at 470 cm\(^{-1}\). This degree of mode softening is the largest found among all of the alkane configurations and suggests that \(\eta^2(C,H)\) and \(\eta^2(H,H)\) configurations can be distinguished with vibrational spectroscopy. Furthermore, the dramatic difference in mode softening between the two configurations may also result in differences in C-H bond cleavage, but future studies of the C-H scission will be needed to confirm this hypothesis.

A pronounced effect is also observed in the \(\eta^1\) configuration of \(n\)-butane where the mode softening associated with the CH\(_2\) group is greater by nearly 100 cm\(^{-1}\) over that associated with the CH\(_3\) group. The percent change in the C-H bond length also reflects the difference in mode softening as the primary (secondary) C-H bond stretches.
by 2.36 (3.08) % from the corresponding gas-phase values. The difference between primary and secondary C-H bonds does not seem to be entirely attributable to differences in H-Pd interactions since those bond lengths differ only by ~ 0.05 Å. In general, the secondary C-H bonds are more easily cleaved than the primary bonds due to hyperconjugation (i.e. resonance stabilization) and it is believed that this effect is responsible for the greater mode-softening of the secondary C-H bond. Therefore, the DFT calculations suggest that cleavage of the secondary C-H bond of n-butane will be more facile than the primary C-H bond. Such a hypothesis based on mode softening and bond stretching will have to be confirmed with future studies of C-H activation barriers for the alkanes.

2.3.3 Dissociation Pathways for \( \eta^2 \) Methane

Understanding the mechanisms and barriers for C-H bond cleavage of alkanes in different bonding configurations (\( \eta^1 \) vs. \( \eta^2 \), primary vs. secondary) will provide important insights for understanding the factors which influence alkane activation on the PdO(101) surface. This information can be subsequently used to explore modifications of the surface to enhance activity for alkane oxidation. Subsequent chapters explore all the possible reaction pathways for ethane to \( n \)-butane while, presented in this section are results for C-H activation of the \( \eta^2 \) methane configuration shown in Figure 2-3 A). The adsorbed CH\(_4\) molecule has two types of C-H bonds that are candidates for cleavage. The first is the non-interacting, upward-oriented C-H bond pointed toward the cus-O atom and the second is one of the two equivalent C-H bonds involved in the \( \eta^2 \) interaction with the cus-Pd atom. The other upward-oriented C-H bond has not been considered since recent DFT studies of H\(_2\) on PdO(101) indicate that the preferred
binding site for an H atom is on top of a *cus*-O atom. Therefore, the first pathway investigated is a simple transfer of the upward-oriented H atom to the adjacent *cus*-O site as shown in Figure 2-6. This pathway yields a large C-H activation barrier of 167 kJ/mol, which suggests that C-H bond cleavage involving the non-interacting H-atom occurs negligibly on the PdO(101) surface.

![Figure 2-6. The DFT predicted pathway for initial C-H bond cleavage of methane on PdO(101) through the surface non-interacting H atom.](image)

In an earlier recent study of H₂ dissociation, a facile dissociation pathway that involves rotation of the H₂ molecule lying parallel to the *cus*-Pd rows to yield a final dissociated H₂ state where one of the H atoms is firmly bound on top of the *cus*-O site was identified. A similar pathway for cleavage of a downward-oriented C-H bond of the adsorbed methane molecule is determined.
Figure 2-7. The DFT predicted pathway for initial C-H bond cleavage of methane on PdO(101) through the H atom involved in the four center $\eta^2$ interaction with a cus-Pd atom.
In this pathway (shown in Figure 2-7), the CH$_4$ molecule first undergoes a rotation and subsequent elongation of the C-H bond, and then dissociates to a final state that is very similar to that found for the first pathway. However, this second pathway results in a much lower barrier of 63.7 kJ/mol, indicating that the $\eta^2$ interaction strongly facilitates C-H bond cleavage. The only difference between the final states in the two pathways is a small rotation of the methyl group, but the energies are nearly degenerate. The final state(s) have been confirmed to be true minima through normal mode analysis but there are very low frequency (~50 cm$^{-1}$) rotational modes involving the methyl species. While the quantitative values for the barriers for methane activation determined with DFT should be taken with caution due to the lack of dispersion interactions, the results clearly show that dative bonding between the alkane molecule and the cus-Pd atom lowers the C-H bond cleavage barrier by more than 100 kJ/mol for CH$_4$. Subsequent studies will incorporate DFT-D implementations to more accurately predict both the adsorption and activation energies for methane and other alkanes on the PdO(101) surface. Once more accurate values incorporating dispersion are known, the CH$_4$ dissociation rates at commercially-relevant temperatures and pressures can be estimated using transition state theory. Finally, the mode softening shows strong dependence for the $\eta^1$ interactions with primary versus secondary carbon groups on $n$-butane, so C-H activation studies of $n$-butane will be helpful in correlating mode softening to preferential C-H activation.
2.4 Summary

The molecular adsorption and dissociation of \textit{n}-butane on a PdO(101) thin film has been investigated using TPRS experiments and DFT calculations. The TPD results reveal that \textit{n}-butane molecules populate a low-coverage state on PdO(101) that is more strongly-bound than \textit{n}-butane molecules physisorbed on Pd(111). This behavior is similar to that seen with smaller alkanes, and arises from the formation of \textit{n}-butane $\sigma$-complexes on PdO(101). The binding energies of the \textit{n}-butane $\sigma$-complexes continues the linear trend reported previously for binding energy vs. chain length relation of \textit{n}-alkane (C$_1$ to C$_3$) $\sigma$-complexes on PdO(101). This $E$ vs. $N$ relation demonstrates that dative bonding produces a similar enhancement in alkane binding on PdO(101) vs. Pd(111) with increasing chain length up to \textit{n}-butane. TPRS results also show that a fraction of the \textit{n}-butane layer undergoes C-H bond cleavage on PdO(101) under the conditions investigated, and that the resulting fragments are completely oxidized by the surface upon continued heating.

DFT calculations confirm that \textit{n}-butane molecules bind relatively strongly on PdO(101) by forming $\sigma$-complexes on the \textit{cus}-Pd rows. The calculations predict that the favored bonding geometry for \textit{n}-butane is an $\eta^1$(2H) configuration in which the \textit{n}-butane molecule lies parallel to the \textit{cus}-Pd row and forms two H-Pd coordinate bonds. Calculations reveal that steric repulsions between the terminal alkyl groups and the surface disrupt the bonding achieved in the $\eta^2$ configurations of \textit{n}-butane, resulting in a strong preference for \textit{n}-butane to adopt the $\eta^1$(2H) configuration along the \textit{cus}-Pd row. In general, this steric effect causes the preferred bonding geometry of alkane $\sigma$-
complexes on PdO(101) to change from $\eta^2$ to $\eta^1$ configurations with increasing chain length, with the $\eta^1$ configurations becoming preferred for molecules larger than propane.

The DFT calculations also demonstrate that the formation of alkane $\sigma$-complexes on PdO(101) weakens the coordinated C-H bonds, making them easier to cleave. Elongation of the coordinated C-H bonds accompanied with significant vibrational-mode softening is also observed. The extent of C-H bond weakening caused by the dative interaction generally correlates with the stability of the alkyl radicals. Additionally, it is observed that coordination with the Pd center lowers the energy barrier for C-H bond cleavage by more than 100 kJ/mol for CH$_4$ adsorbed in the $\eta^2$ configuration. Given the more pronounced C-H bond weakening seen for the larger alkanes, it is anticipated that the dative bonding interaction will lower the C-H bond cleavage barriers for these molecules to an even greater extent than that predicted for methane. A key finding is that the formation of relatively strongly-bound $\sigma$-complexes on PdO(101) serves to electronically activate alkane C-H bonds in addition to prolonging the surface lifetimes of these reactive precursors. These results suggest the possibility that adsorbed $\sigma$-complexes play a general role as precursors for alkane activation on transition metal oxide surfaces.
CHAPTER 3
DISPERSION-CORRECTED DENSITY FUNCTIONAL THEORY CALCULATIONS OF
THE MOLECULAR BINDING OF \( n \)-ALKANES ON Pd(111) AND PdO(101)

3.1 Motivation

Understanding the interactions of alkanes with the surfaces of transition metals and transition metal oxides is essential for developing robust computational models of alkane activation by heterogeneous catalysts. In general, the most reactive surfaces for alkane activation are those on which initial C-H bond cleavage occurs predominantly from a molecularly adsorbed state of the alkane, \( i.e. \), a precursor-mediated mechanism.\(^6\)\(^1\) For such systems, proper representation of the alkane-surface interactions is important for ensuring accuracy and may be critical for accurately predicting bond selectivity in alkane activation. Conventional DFT fails to capture the dispersion forces which dominate the interactions between alkanes and transition metal surfaces. As a result, conventional DFT significantly underestimates the adsorption energies of alkanes. Advances in describing molecule-surface dispersion interactions could significantly improve the quantitative accuracy of DFT calculations for describing alkane adsorption and activation on solid surfaces.

Investigations of the surface chemistry of PdO are motivated largely by a need to better understand applications of Pd-catalyzed oxidation processes. Palladium catalysts exhibit high activity for alkane oxidation under oxygen-rich conditions, and are well-suited for applications of catalytic combustion, exhaust gas remediation and selective oxidation processes. Studies of supported catalysts provide strong evidence that bulk

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Reprinted (adapted) from the Journal of Chemical Physics, Volume 136, Issue 5, A. Antony, C. Hakanoglu, A. Asthagiri, J.F. Weaver. Dispersion-corrected density functional theory calculations of the molecular binding of \( n \)-alkanes on Pd(111) and PdO(101), Pages 054702 (1-9). Copyright © 2012 with permission from American Institute of Physics and the authors.
PdO is highly active for alkane activation and that the formation of PdO is responsible for the high activity of Pd catalysts toward alkane oxidation under oxygen-rich conditions.\(^9\) Consistent with these observations, it has been found that the activation of propane and higher alkanes is highly facile on the PdO(101) surface, with initial C-H bond cleavage of propane, \(n\)-butane and \(n\)-pentane occurring below about 200 K under ultrahigh vacuum (UHV) conditions.\(^{78,96}\) Based on experimental measurements as well as conventional DFT calculations, it has been shown that \(n\)-alkanes form \(\sigma\)-complexes on PdO(101) by datively bonding with coordinatively unsaturated (cus) Pd atoms of the PdO surface, and that the \(\sigma\)-complexes serve as precursors for initial C-H bond cleavage.\(^{78,79,96}\) The formation of \(\sigma\)-complexes enhances the binding energies of \(n\)-alkanes on PdO(101) by \(~25\) kJ/mol over that observed on Pd(111), and produces a non-zero intercept in the linear relation between the binding energy and chain length of \(n\)-alkanes adsorbed on PdO(101).\(^{79,96}\) The dative interactions between alkanes and PdO(101) also weaken the Pd-coordinated C-H bonds, making them easier to cleave.

Conventional DFT predicts that \(n\)-alkanes bind more strongly on PdO(101) than Pd(111), in agreement with experimental findings. Evidence of \(\sigma\)-complex formation on PdO(101) also comes from DFT predicted changes in the electronic states and charge density distribution upon alkane adsorption, along with the preferred binding configurations and softening of vibrational modes associated with the Pd coordinated C-H bonds.\(^{79,96}\) Although conventional DFT provides strong evidence of alkane \(\sigma\)-complex formation on PdO(101), the calculations significantly underestimate the alkane binding energies on PdO(101) as well as Pd(111) because dispersion interactions are not properly represented.
Incorporating dispersion into DFT calculations is a field of active research with different approaches to address the issue. A practical approach to this problem is given by the DFT-D method developed by Grimme and coworkers. The DFT-D method treats dispersion by summing over parameterized $C_6$ atom-pair interactions and then adds the results to the self-consistent energy determined using DFT. The first versions of the DFT-D method (DFT-D1 and 2) provide an accurate description of the binding in large molecules and complexes, but tend to overestimate the adsorption energies of molecules on metal surfaces. In these calculations, the $C_6$ parameters are derived from atomic properties and estimated for atom-pairs using empirical combining formulas. Tonigold and Gross have recently shown that the DFT-D method predicts more accurate adsorption energies of aromatics on noble metal surfaces when the $C_6$ parameters are derived using a hybrid QM:QM approach rather than being deduced from atomic properties. This finding highlights the importance of accounting for the local bonding environment when modeling dispersion interactions. Grimme et al. have recently reported a third version of the DFT-D method, denoted as DFT-D3, which is shown to provide higher accuracy and broader applicability than the earlier versions. Key improvements included in the DFT-D3 method are more accurate estimates of the $C_6$ parameters from time-dependent DFT calculations, and the use of fractional coordination numbers to allow the $C_6$ parameters to vary with the local chemical environment. Initial calculations reveal that the DFT-D3 method provides a more accurate description of molecular adsorption onto metal surfaces. This result is encouraging as it suggests that the DFT-D3 approach has potential for providing chemical accuracy in describing molecule-surface interactions.
In this chapter, the molecular binding of \( n \)-alkanes on Pd(111) and PdO(101) are investigated and compared using conventional DFT and the DFT-D3 method. It is observed that calculations using the DFT-D3 technique provide good agreement with experimentally-determined desorption energies of \( n \)-alkanes adsorbed on both Pd(111) and PdO(101). The DFT-D3 calculations also predict that the enhanced binding of alkanes on PdO(101) compared to Pd(111) arises predominantly from dative bonding with the \textit{cus}-Pd atoms of the oxide surface.

### 3.2 Computational Details

Conventional and dispersion-corrected DFT (DFT and DFT-D3 respectively) calculations presented in this chapter are performed employing the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{84-87} using projector augmented wave (PAW) pseudopotentials\textsuperscript{39,89} provided in the VASP database. Parameters for the calculations are similar to those used in earlier studies of the PdO(101) surface.\textsuperscript{79,88,96} The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is used\textsuperscript{33} with a plane wave cutoff of 400 eV. Total energy calculations are done using the residual minimization method with direct inversion in the iterative subspace for electronic relaxations accelerated using Methfessel-Paxton Fermi-level smearing with a Gaussian width of 0.1 eV.\textsuperscript{101} Ionic forces are relaxed using a limited memory Broyden-Fletcher-Goldfarb-Shanno optimization method\textsuperscript{59} until the total forces on all unconstrained atoms are less than 0.03 eV/Å. The empirically determined dispersion energy \( (E_{\text{disp}}) \) used in the DFT-D3 formulation is given by Equation 3-1,\textsuperscript{48} where the pairwise interactions are summed over all the atoms within a cutoff radius of 50 Å. The additive term \( (E_{\text{disp}}) \) is a function of \( n \)^{th} order inter-nuclear distances \( (r_{AB}^{-n}) \), dispersion coefficients \( (C_{n}^{AB}) \) that have been
computed *ab initio* by time dependent DFT, a scaling factor \( (s_n) \) that ensures asymptotic exactness, and a damping function \( (f_{d,n}(r)) \). The parameters have been directly taken from the most recent implementation of dispersion in DFT calculations by Grimme *et al.*

\[
E_{\text{disp}} = -\frac{1}{2} \sum_{AB} \left[ s_6 \frac{C_{6}^{AB}}{r_{6}^{AB}} f_{d,6}(r_{AB}) + s_8 \frac{C_{8}^{AB}}{r_{8}^{AB}} f_{d,8}(r_{AB}) \right]
\]  

(3-1)

The theoretical model for Pd(111) is represented by a \( 4 \times 4 \) unit cell that is comprised of three layers of Pd atoms, with the bottom layer fixed. A vacuum spacing of 18 Å is maintained normal to the surface to avoid spurious interactions in this direction. A \( 2 \times 2 \times 1 \) Monkhorst-Pack \( k \)-point mesh is used in the calculations. Using finer mesh sizes or increasing the number of layers does not result in significant changes in adsorption energy \(< 0.1 \text{ kJ/mol})\). Calculations with Pd(111) are based on a single alkane molecule adsorbed in the \( 4 \times 4 \) unit cell, which is equivalent to an alkane coverage of 0.0625 ML. Based on prior experimental investigations, it is estimated that the saturation coverages of \( n \)-alkanes \( (N < 5) \) adsorbed on Pd(111) lie between 0.14 and 0.21 ML.

Figure 3-1 depicts the stoichiometric PdO(101) surface that is investigated in this study. Experimentally, a PdO(101) film is grown on a Pd(111) substrate at 500 K by oxidizing the metal surface in UHV using an oxygen atom beam. The resulting PdO(101) film is \(~13 \) Å thick and contains \(~3 \) ML of oxygen atoms, where 1 ML is equal to the Pd(111) surface atom density of \( 1.53 \times 10^{15} \) cm\(^{-2}\). Bulk crystalline PdO has a body-centered tetragonal structure and consists of square planar units of Pd atoms fourfold coordinated with oxygen atoms. The bulk-terminated PdO(101) surface is
defined by a rectangular unit cell, where the $a$ and $b$ lattice vectors coincide with the $[010]$ and $[\bar{1}01]$ directions of the PdO crystal, respectively. The stoichiometric PdO(101) surface consists of alternating rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the $a$ direction shown in Figure 3-1. Thus, half of the surface O and Pd atoms are coordinatively unsaturated ($cus$). The side view of PdO(101) shows that the coordinative environment associated with each $cus$-Pd atom resembles a square planar Pd complex with a coordination vacancy directed away from the surface and three oxygen ligands, one of which is a $cus$-O atom.

Figure 3-1. Model representation of the stoichiometric PdO(101) surface. Coordinatively saturated ($4f$) and coordinatively unsaturated ($cus$) Pd and O atoms have been labelled. The $\bar{a}$ and $\bar{b}$ directions correspond to the $[010]$ and $[\bar{1}01]$ crystallographic directions of bulk PdO.

The PdO(101) model used in this computational study is the same as that used in earlier studies and consists of four layers corresponding to a thickness of ~9 Å.
Previous work has shown that this thickness is sufficient to accurately model the experimental PdO(101) film on Pd(111). The PdO(101) model is strained to match the structure reported by LEED experiments \( (a = 3.057 \, \text{Å}, \ b = 6.352 \, \text{Å}) \).\(^{19}\) A vacuum spacing of 20 Å is maintained normal to the surface and a \( 4 \times 2 \times 1 \) \( (2 \times 4 \times 1) \) Monkhorst-Pack \( k \) point mesh has been used for the \( 4 \times 1 \) \( (2 \times 2) \) unit cell size.

Binding energies are reported based on a single alkane molecule adsorbed on the model PdO(101) surface(s) for which the alkane coverage is equal to 0.0825 ML. The simulated coverage is close to experimental estimates of the saturation coverage(s) (~0.085 to 0.10 ML) of alkane \( \sigma \)-complexes \( (N = 1 \text{ to } 5) \) on PdO(101).\(^ {78, 79, 96} \)

Calculations reveal that the alkane \( \sigma \)-complexes are separated by more than 6 Å at 0.0825 ML and interact only weakly with one another as a result. Finally, normal mode analysis were performed to ensure that the relaxed configurations of alkanes on PdO(101) and Pd(111) possess only real vibrational frequencies and are thus true minima. The vibrational modes are calculated by fixing the surface atoms while leaving the chemisorbed molecule unconstrained.

To make comparisons with experimental desorption data, the adsorption/binding energy \( (E) \) and the activation energy for desorption \( (E_A) \), which is referred to as the “desorption energy” needs to be distinguished. Tosoni and Sauer have presented a similar approach for comparing computed binding energies with measured desorption activation energies.\(^ {100} \) The adsorption/binding energy \( (E) \) is defined as the difference between the sum of total energies (electronic plus dispersion) for the isolated molecule \( (E_{iso}) \) and bare surface \( (E_{bare}) \) with that of the chemisorbed molecule/surface system \( (E_{chemisorb}) \) as seen in Equation 3-2.
\[ E = [E_{\text{bare}} + E_{\text{iso}}] - E_{\text{chemisorb}} \] (3-2)

The binding energy thus represents the total molecule-surface interaction energy referenced to the bottom of the adsorption well as determined by DFT or DFT-D3. Transition state theory provides a relation between the activation energy and the internal energy change of activation.\textsuperscript{104} Note that the transition state for desorption is taken as a gas-phase molecule less one translational degree of freedom. According to transition state theory, the desorption energy \( E_A \) is given by Equation 3-3.

\[ E_A = \Delta E_{TS} + RT \] (3-3)

The quantity \( \Delta E_{TS} \) represents the internal energy change of activation and is given by Equation 3-4.

\[ \Delta E_{TS} = \frac{5}{2} RT + \Delta ZPE + \Delta E_v + E \] (3-4)

In Equation 3-4, \( \Delta ZPE \) represents the difference in zero-point energy between the transition state and the initial adsorbed state, \( \Delta E_v \) represents the change in average vibrational energy, \( E \) represents the binding energy and \( \frac{5}{2} RT \) is equal to the difference in translational plus rotational energy for a non-linear molecule in the desorption transition state vs. the adsorbed state. The zero-point energies and average vibrational energies are evaluated using normal mode vibrational frequencies determined for the gas-phase molecules and each adsorbed state. The average energies are calculated at the peak desorption temperatures observed in TPD experiments. The difference between \( E \) and \( E_A \) is less than 3 kJ/mol for \( N = 1 \) to 4, and is highest (~4.7 kJ/mol) for
*n*-pentane adsorbed on PdO(101) but still constitutes less than 5% of the total binding energy.

It is observed that interactions between adsorbed alkanes have a negligible effect on the computed binding energies in the calculations presented here. For example, interactions between the periodic images of *n*-pentane molecules in a 4 × 1 vs. an 8 × 1 unit cell of PdO(101) were compared by calculating the energy after removing the surface and allowing the molecules to relax. The comparison reveals that intermolecular interactions contribute only about 0.2 kJ/mol to the total binding energy of *n*-pentane adsorbed on the 4 × 1 model of PdO(101). Similar results were obtained for *n*-pentane adsorbed in the 4 × 4 unit cell of Pd(111). Thus, the binding energies computed in this study represent the intrinsic alkane-surface interaction energies with a high degree of accuracy. The finding is consistent with experimental TPD data which shows that the temperature of the monolayer TPD peak remains approximately constant with increasing alkane coverage, even after the state in the first-layer approach saturation.78, 79, 96

### 3.3 Experimental Details

Separate studies report temperature programmed desorption (TPD) spectra of *n*-alkanes (N = 1 to 4) on Pd(111) and PdO(101) and estimated the desorption energies of these species from the TPD spectra. The reader may refer to the section titled ‘Experimental Observations’ in chapter 2 and prior papers for details, results and interpretation of the experiments.78, 79, 96 In this chapter, experimental estimates of the CH₄ through *n*-C₄H₁₀ desorption energies on Pd(111) and PdO(101) are compared with values computed from DFT and DFT-D3. New experimental estimates of the *n*-pentane
desorption energies on Pd(111) and PdO(101) are also included, which were obtained following the same procedures as utilized in previous studies. As expected, the \( n \)-butane and \( n \)-pentane TPD spectra (not shown) are qualitatively similar for both surfaces, and \( n \)-pentane desorbs at slightly higher temperatures than \( n \)-butane. Compared with smaller alkanes, a greater fraction of \( n \)-pentane dissociates on PdO(101) rather than desorbing during the TPD experiments. Dissociation of \( n \)-pentane on Pd(111) occurs to an immeasurable extent under the conditions studied. Dissociation yields of 41\%, 64\% and 72\% are estimated for propane, \( n \)-butane and \( n \)-pentane on PdO(101) at saturation of the molecular precursor state.

Redhead analysis was used to estimate desorption energies from the alkane TPD spectra at low alkane coverages.\(^{78,79,96}\) For the data obtained from Pd(111), the same pre-factors as reported by Tait et al.\(^ {93}\) were used for \( n \)-alkane desorption from Pt(111) which those authors estimated using an inversion-optimization method. For PdO(101), desorption energies are reported for only the more strongly-bound alkane \( \sigma \)-complex state and utilize maximum values of the desorption pre-factors for the Redhead analysis, where the maximum pre-factors are estimated from formulas based on transition state theory for the desorption of an immobile adsorbate.\(^ {93}\) Evidence has been previously presented that the maximum desorption pre-factors are appropriate for estimating the desorption energies of alkane \( \sigma \)-complexes on PdO(101).\(^ {79,96}\)

3.4 Results and Discussion

3.4.1 Alkane Binding on Pd(111)

The binding of \( n \)-alkanes on the Pd(111) surface are investigated using both conventional DFT and DFT-D3. It is observed that \( n \)-alkanes can bind in several stable
configurations on Pd(111) and that these states have similar binding energies. For example, conventional DFT predicts small binding energies of 2.7, 2.4 and 2.4 kJ/mol, respectively, for CH$_4$ adsorbed over the atop site, the fcc hollow site and the hcp hollow site. DFT-D3 predicts a similar trend in the preferred binding sites of CH$_4$ on Pd(111). From DFT-D3, binding energies of 23.7, 22.5 and 22.8 kJ/mol are determined for CH$_4$ adsorbed at the atop, fcc hollow and hcp hollow sites, respectively. The binding configurations of larger alkanes on Pd(111) are also only weakly dependent on the lateral position of the molecule within the surface unit cell, indicating that the alkane-Pd(111) interaction is relatively flat with respect to molecular displacements parallel to the surface plane.

The larger alkanes achieve optimal binding on Pd(111) by aligning their molecular axes parallel to the surface plane. Such configurations bring each CH$_x$ group close to the surface, thus enabling each group to experience a similar attractive interaction with the solid. It is noted that n-alkanes in “flat-lying” and “staggered” configurations have similar binding energies on Pd(111), at least up to n-pentane. In a flat-lying configuration, the molecular plane of the n-alkane lies approximately parallel to the surface such that the distance between the surface and each CH$_x$ group is nearly the same. A staggered configuration can be obtained by rotating a flat-lying n-alkane by 90° about its molecular axis.

Favored configurations of propane on Pd(111) are shown in Figure 3-2 to highlight the differences between flat-lying and staggered configurations. The binding energies predicted by DFT-D3 vary from 51.1 to 54.1 kJ/mol (< 6%) among the preferred configurations of C$_3$H$_8$ on Pd(111), demonstrating that the flat-lying and
staggered configurations are similar in energy even though the staggered configurations put the central carbon atom farther from the surface than does the flat-lying configuration. A key point is that the alkane-Pd(111) interaction has a relatively small corrugation lateral to the surface according to the DFT and DFT-D3 calculations.

Figure 3-2. Propane configurations on PdO(101) determined using DFT-D3. A) Flat lying configuration with an adsorption energy of 53.1 kJ/mol. B, C) Staggered configurations with adsorption energies of 54.1 and 51.1 kJ/mol, respectively.

Figure 3-3 shows \(n\)-alkane desorption energies on Pd(111) as a function of the alkane chain length as estimated from experimental TPD data and computed using conventional DFT as well as DFT-D3. Table 3-1 lists the experimentally-determined and computed alkane binding and desorption energies on Pd(111). For convenience, the desorption energies of the global minima are considered rather than weighted averages for comparison with the desorption energies estimated from experiment. This approach is reasonable because DFT predicts small energy differences among the stable
adsorption geometries of a given alkane. As the chain length increases to \( N = 5 \), the experimental desorption energies increase linearly from \( \sim16 \) to \( 74 \) kJ/mol, with each CH\(_x\) group contributing about \( 14 \) kJ/mol to the total desorption energy. Dispersion interactions are primarily responsible for the binding of alkanes on Pd(111), but are not captured by conventional DFT. As a result, conventional DFT significantly underestimates the \( n \)-alkane binding energies on Pd(111).

![Graph showing comparison of desorption energies vs. chain length of \( n \)-alkanes on Pd(111) computed by conventional DFT and DFT-D3 against that determined experimentally.](image)

According to conventional DFT, the desorption energies of \( n \)-alkanes on Pd(111) increase from \( \sim1 \) to \( 10.9 \) kJ/mol as the chain length increases to \( n \)-pentane, which corresponds to only \( \sim2.5 \) kJ/mol per CH\(_x\) group. Notice that the absolute difference
between the experimental and computed desorption energy increases considerably with increasing chain length (Table 3-1, Figure 3-3). The percent difference between the experimental and DFT-derived desorption energies remains nearly constant at ~88% for \( n \)-alkanes on Pd(111) up to \( N = 5 \). The small binding energies determined using conventional DFT demonstrate that electronic interactions between alkanes and Pd(111) are weak, and thus make only a minor contribution to the total energies in this system.

Table 3-1. Desorption energies of various \( n \)-alkanes on the Pd(111) surface determined experimentally (\( E_{A,exp} \)) and computed using conventional DFT (\( E_{A,DFT} \)) and DFT-D3 (\( E_{DFT-D3}, E_{A,DFT-D3} \)). \( E_{disp} \) represents the contribution of the dispersion energy in the relaxed configuration determined by DFT-D3 while \( E_{elec} \) represents the contribution of electronic interactions. A negative \( E_{elec} \) value indicates that the DFT-D3 relaxed configuration experiences repulsive interactions. All energies are given in units of kJ/mol.

<table>
<thead>
<tr>
<th>Alkane</th>
<th>( E_{A,exp} )</th>
<th>( E_{A,DFT} )</th>
<th>( E_{DFT} )</th>
<th>( E_{A,DFT-D3} )</th>
<th>( E_{DFT-D3} )</th>
<th>( E_{elec} )</th>
<th>( E_{disp} )</th>
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<tr>
<td>( \text{CH}_4 )</td>
<td>16.4</td>
<td>1.1</td>
<td>2.7</td>
<td>23.6</td>
<td>23.7</td>
<td>-1.8</td>
<td>25.5</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>30.3</td>
<td>3.6</td>
<td>4.4</td>
<td>40.8</td>
<td>39.6</td>
<td>-0.2</td>
<td>39.8</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_8 )</td>
<td>44.5</td>
<td>6.0</td>
<td>6.6</td>
<td>55.9</td>
<td>54.1</td>
<td>1.9</td>
<td>52.2</td>
</tr>
<tr>
<td>( n-\text{C}<em>4\text{H}</em>{10} )</td>
<td>56.6</td>
<td>6.8</td>
<td>8.1</td>
<td>68.8</td>
<td>67.2</td>
<td>2.0</td>
<td>65.2</td>
</tr>
<tr>
<td>( n-\text{C}<em>5\text{H}</em>{12} )</td>
<td>73.8</td>
<td>10.9</td>
<td>11.9</td>
<td>86.9</td>
<td>84.5</td>
<td>4.8</td>
<td>79.7</td>
</tr>
</tbody>
</table>

* Energies are reported in kJ/mol \( C_N\text{H}_{2N+2} \)

Including dispersion interactions in the DFT calculations improves the agreement between the computed and experimentally-determined desorption energies of alkanes on Pd(111) (Figure 3-3, Table 3-1). The desorption energies computed using DFT-D3 increase from 23.6 to 86.9 kJ/mol with increasing chain length to \( n \)-pentane, and each \( \text{CH}_x \) group contributes an average of 15.8 kJ/mol to the total desorption energy. The computed \( E_A \) vs. \( N \) relation is linear, in agreement with the experimental results, but the computed energies lie above the experimentally-determined energies by about 10.9 ±
2.3 kJ/mol. This nearly constant offset causes the computed $E_A$ vs. $N$ line to have a non-zero intercept of 8.8 kJ/mol. For comparison, the experimental $E_A$ vs. $N$ relation has an intercept of only 2 kJ/mol. In the present calculations, the large, non-zero intercept arises mainly from small corrugation in the alkane-Pd(111) interaction which causes the average binding energy per CH$_x$ group to decrease slightly with increasing chain length. Note that the measured energies are compared with desorption energies computed for the global minimum of each alkane. The DFT-D3 derived desorption energies would decrease slightly (< 1 kJ/mol) if appropriate averages were computed over the various configurations of each alkane but the predicted desorption energies would still be overestimated. The percent differences between the experimental and DFT-D3 derived desorption energies improve as the alkanes become larger, decreasing from 44% to 18% with increasing chain length from $N = 1$ to 5. Overall, the calculations show that DFT-D3 provides more accurate values of the desorption energies of $n$-alkanes on Pd(111) compared with conventional DFT.

Comparison of the binding energies computed using conventional DFT vs. DFT-D3 suggests that the dispersion energy represents more than 88% of the total binding energy of $n$-alkanes on Pd(111). However, it is observed that the geometrical configurations differ slightly between the DFT and DFT-D3 results. Specifically, dispersion pulls the molecules closer to the surface, thus moving the alkanes away from the separation at which the electronic energy alone is optimized. For example, the C-Pd distances for CH$_4$ adsorbed on an atop site of Pd(111) are 3.62 Å and 2.95 Å from conventional DFT and DFT-D3, respectively. To explore the consequences of this geometrical change, the total binding energy determined from DFT-D3 ($E_{DFT-D3}$) were
decomposed into separate dispersion and electronic components, designated as $E_{\text{disp}}$ and $E_{\text{elec}}$, respectively, where $E_{\text{DFT-D3}} = E_{\text{disp}} + E_{\text{elec}}$. Here, the electronic energy $E_{\text{elec}}$ is equal to the energy determined from a single-point DFT calculation (i.e., excluding dispersion) applied to the minimum energy configuration determined using DFT-D3. The difference between $E_{\text{DFT-D3}}$ and $E_{\text{elec}}$ gives the dispersion energy $E_{\text{disp}}$.

From this definition, the electronic energy contains contributions from bonding interactions as well as Coulombic and other electrostatic interactions.

The energy deconvolution shows that the decrease in alkane-Pd(111) distance causes the electronic energies to fall below the optimal values determined using conventional DFT. The electronic energies $E_{\text{elec}}$ decrease by $5.4 \pm 1.1$ kJ/mol when dispersion is included in the calculations, and become slightly negative for methane and ethane (Table 3-1). Since the electronic energy is no longer optimized, dispersion makes an even greater contribution to the total binding energy than suggested above.

The analysis shows that the dispersion energy accounts for $\sim 99 \pm 5\%$ of the total binding energy of $n$-alkanes on Pd(111) up to $N = 5$ for the optimized configurations determined using DFT-D3.

Decomposing the total binding energy into dispersion and electronic components also helps to clarify the origin of the non-zero intercept of the computed $E$ vs. $N$ relation. A linear $E$ vs. $N$ relation is observed for physisorbed alkanes on close-packed surfaces because the molecules lie flat on the surface and each CH$_2$ group makes roughly the same contribution to the total desorption energy. By taking into account the increase in desorption pre-factor with increasing $N$, Tait et al.$^{93, 105, 106}$ have shown that the intercept
of the measured $E$ vs. $N$ relations is relatively small for $n$-alkanes adsorbed on close-packed surfaces; an intercept of only 2 kJ/mol is found for $n$-alkanes on Pd(111). The small intercept suggests that the CH2 groups and CH3 end-groups experience similar interaction energies with the surface. The additional H-atoms may slightly enhance the binding of CH3 vs. CH2 groups to the surface, producing a non-zero, yet small, intercept.

The present analysis shows that the relation between $E_{\text{disp}}$ and $N$ is linear for alkanes on Pd(111) but has an intercept of 12.3 kJ/mol, demonstrating that the large intercept in the computed $E_A$ vs. $N$ relation arises mainly from a characteristic of the molecule-surface dispersion interaction. It is found that the computed dispersion energy per CHx group is slightly molecule dependent, with the average energy per CHx group decreasing with increasing chain length. For example, the dispersion energy for CH4 on Pd(111) is 25.5 kJ/mol while that for ethane is 39.9 kJ/mol which is equivalent to about 20 kJ/mol for each CH3 group. Likewise, the dispersion energy of $n$-pentane on Pd(111) is equivalent to a dispersion energy of ~16 kJ/mol per CHx group. These differences are the result of small corrugation in the alkane-Pd(111) interaction. In particular, the lack of registry between the molecules and the surface atoms places the CHx groups in increasingly less favorable binding sites as the chain length increases, particularly in moving from methane to ethane. The differences in dispersion energy per CHx group among the $n$-alkanes may indicate that the pairwise additive treatment of dispersion interactions results in a slight overestimation of the actual molecule-surface corrugation, thereby producing a non-zero intercept in the computed $E_A$ vs. $N$ relation. The error associated with the corrugation is rather small and indeed the overall agreement
between the experimental and DFT-D3 derived desorption energies is quite good and improves for larger alkanes.

3.4.2 Alkane Binding on PdO(101)

The binding of \( n \)-alkanes on the PdO(101) surface were also investigated using both conventional DFT and DFT-D3. Alkanes form \( \sigma \)-complexes on PdO(101) by coordinating with \( cus \)-Pd atoms of the surface (Figure 3-1). As discussed previously, \( \sigma \)-complex formation produces a nearly constant enhancement of \( \sim 25 \) kJ/mol in the desorption energies of \( n \)-alkanes on PdO(101) vs. Pd(111).\(^{79,96}\) The \( n \)-alkane desorption energies on PdO(101) and Pd(111) are compared in more detail below.

According to conventional DFT, the alkane \( \sigma \)-complexes on PdO(101) adopt \( \eta^1 \) and \( \eta^2 \) configurations in which one or more of the CH\(_x\) groups coordinates with \( cus \)-Pd atoms. While each alkane can bind on PdO(101) in several stable configurations, a trend had been identified using conventional DFT wherein the preferred configuration changes from \( \eta^2 \) to \( \eta^1 \) as the alkane chain length increases above \( N = 3 \).\(^{96}\)

In the present study, it is revealed that DFT and DFT-D3 each predict the same trends in the preferred binding configurations of alkanes on PdO(101). The global minima for methane and ethane are \( \eta^2 \)(H, H) configurations in which a H-C-H bond angle is centered over a \( cus \)-Pd atom and is aligned such that each H-atom which coordinates with the Pd atom resides along the \( cus \)-Pd row. Two H-atoms of a CH\(_x\) group dative bond with a \( cus \)-Pd atom in the \( \eta^2 \)(H, H) configurations. Alkanes larger than propane strongly prefer to bind on PdO(101) in \( \eta^1 \) configurations wherein the molecule aligns along the \( cus \)-Pd row and single H-Pd dative bonds form at different
Propane is a special case because an $\eta^2$ configuration and two $\eta^1$ configurations are nearly energetically degenerate.

**Figure 3-4.** Propane configurations on PdO(101) determined using DFT-D3. A) Staggered $\eta^1$(2H) configuration with adsorption energy of 72.0 kJ/mol. B) Flat lying $\eta^1$(2H) configuration with adsorption energy of 69.2 kJ/mol. C) $\eta^2$(H,H) configuration with adsorption energy of 70.0 kJ/mol. D) Staggered $\eta^1$(H) configuration with binding energy of 62.1 kJ/mol.

Figure 3-4 depicts the energetically preferred configurations of propane $\sigma$-complexes on PdO(101). DFT-D3 predicts that the staggered $\eta^1$(2H) (st) configuration shown in Figure 3-4 A) has a binding energy of 72.0 kJ/mol and is the most stable configuration of propane on PdO(101). The notation “2H” is used to specify that two H-
Pd dative bonds form in this $\eta^1$ complex. Two other configurations lie very close in energy to the $\eta^1(2H)$ ($st$) configuration. From DFT-D3, it is found that the flat-lying $\eta^1(2H)$ ($fl$) configuration (Figure 3-4 B)) and the $\eta^2(H, H)$ configuration (Figure 3-4 C)) have binding energies of 69.2 and 70.0 kJ/mol, respectively. Considering the small energy difference, transitions between the $\eta^1(2H)$ ($fl$) and $\eta^1(2H)$ ($st$) configurations are likely facile. Finally, Figure 3-4 D) shows an $\eta^1(H)$ configuration in which the propane molecule forms a single H-Pd dative bond at the CH$_2$ group and achieves a binding energy of 62.1 kJ/mol according to DFT-D3. The $\eta^1(H)$ configuration is less stable than the $\eta^1(2H)$ and $\eta^2(H, H)$ configurations, but may be accessible at moderate temperature and high coverages. Including the $\eta^1(H)$ configuration in Figure 3-4 serves to illustrate that propane and indeed larger alkanes can bind in several configurations on PdO(101) and clarifies the characteristic energy differences among these states.

Figure 3-5 shows the desorption energies of $n$-alkanes on PdO(101) estimated from experimental TPD data as well as computed using both DFT and DFT-D3. Table 3-2 also lists the binding and desorption energies of $n$-alkanes on PdO(101) up to $n$-pentane. Conventional DFT underestimates the alkane binding energies on PdO(101) by a similar amount as found for Pd(111). Including dispersion in the calculations causes the binding energies to increase, and produces excellent agreement between the computed and experimental desorption energies. The DFT-D3 derived desorption energies increase from 40.1 to 112.1 kJ/mol, while the experimental energies vary from 42 to 98 kJ/mol with increasing chain length from $N = 1$ to 5. The computed and measured desorption energies agree to within better than 2.3 kJ/mol (< 5%) for CH$_4$.
through \( n\)-C\(_4\)H\(_{10}\). For \( n\)-pentane, the desorption energy predicted by DFT-D3 is 14.1 kJ/mol, or \(~14\%\), greater than the value estimated from TPD data.

Figure 3-5. Comparison of desorption energies vs. chain length of \( n\)-alkanes on PdO(101) computed by conventional DFT and DFT-D3 against that determined experimentally.

The larger difference for \( n\)-pentane relative to the smaller alkanes may arise from difficulties in accurately estimating the \( n\)-pentane desorption energy from the measured TPD spectra. Compared with the smaller alkanes, a greater fraction of the \( n\)-pentane \( \sigma\)-complexes dissociates rather than desorbs in the \( n\)-pentane TPD feature (\( \alpha_1\) peak) that is considered in estimating the alkane desorption energies.\(^{78, 79, 96}\) This behavior could lead to an underestimation of the \( n\)-pentane desorption energy on PdO(101) since the
α\textsubscript{1} TPD peak for \textit{n}-pentane becomes evident only at coverages at which more weakly-bound states are also populated and desorb at low temperatures. Overall, the agreement between the measured desorption energies and those computed using DFT-D3 is excellent for the \textit{n}-alkanes on PdO(101) that have been examined.

Table 3-2. Desorption energies of various \textit{n}-alkanes on the PdO(101) surface determined experimentally (\(E_{A,\text{exp}}\)) and computed using conventional DFT (\(E_{\text{DFT}}, E_{A,\text{DFT}}\)) and DFT-D3 (\(E_{\text{DFT-D3}}, E_{A,\text{DFT-D3}}\)). \(E_{\text{disp}}\) represents the contribution of the dispersion energy in the relaxed configuration determined by DFT-D3 while \(E_{\text{elec}}\) represents the contribution of electronic interactions.

<table>
<thead>
<tr>
<th>Alkane</th>
<th>(E_{\text{A,exp}})</th>
<th>(E_{A,\text{DFT}})</th>
<th>(E_{\text{DFT}})</th>
<th>(E_{A,\text{DFT-D3}})</th>
<th>(E_{\text{DFT-D3}})</th>
<th>(E_{\text{elec}})</th>
<th>(E_{\text{disp}})</th>
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<tr>
<td>CH\textsubscript{4}</td>
<td>42</td>
<td>15.7</td>
<td>16.3</td>
<td>40.1</td>
<td>40.7</td>
<td>15.6</td>
<td>25.1</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>56</td>
<td>20.6</td>
<td>21.0</td>
<td>56.4</td>
<td>56.7</td>
<td>19.4</td>
<td>37.3</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>72</td>
<td>28.2</td>
<td>27.5</td>
<td>69.7</td>
<td>72.0</td>
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<tr>
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<td>87.7</td>
<td>86.2</td>
<td>27.9</td>
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</tr>
<tr>
<td>\textit{n}-C\textsubscript{5}H\textsubscript{12}</td>
<td>98</td>
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<td>39.6</td>
<td>112.1</td>
<td>107.7</td>
<td>39.2</td>
<td>68.5</td>
</tr>
</tbody>
</table>

* Energies are reported in kJ/mol C\textsubscript{N}H\textsubscript{2N+2}

Following the approach described above, the DFT-D3 derived binding energies for \textit{n}-alkanes adsorbed on PdO(101) are decomposed into separate dispersion and electronic components (Table 3-2). This analysis shows that electronic interactions make a significant contribution to the binding of alkanes on the oxide surface, with the electronic energy representing between 32\% and 39\% of the total binding energy of \textit{n}-alkanes on PdO(101). As observed for Pd(111), dispersion pulls the alkane molecules closer to the PdO(101) surface, but the decrease in molecule-surface separation is smaller for alkanes on PdO(101) than Pd(111). For example, the C-Pd distances are 2.54 and 2.44 Å for the \(\eta^2\) CH\textsubscript{4} complex on PdO(101) according to DFT vs. DFT-D3, respectively, corresponding to a change of only 0.1 Å. In addition, the H-C-H bond angles increase by between 1 and 1.5°. Due to the small change in the molecular
configurations, the $E_{elec}$ values for $n$-alkanes on PdO(101) agree well with the binding energies determined from conventional DFT for the relaxed configurations (Table 3-2).

The calculations also predict that vibrational modes associated with the Pd-coordinated C-H bonds soften to a greater extent for the $\eta^2$ configurations predicted by DFT-D3 vs. DFT. Using conventional DFT, the formation of the $\eta^2$ CH$_4$ complex on PdO(101) is predicted to cause red-shifts of 206 cm$^{-1}$, 166 cm$^{-1}$ and 106 cm$^{-1}$ in an asymmetric stretch, a symmetric stretch and an asymmetric bend, respectively. These red-shifts increase to 251 cm$^{-1}$, 211 cm$^{-1}$ and 120 cm$^{-1}$ for the relaxed $\eta^2$ CH$_4$ complex determined using DFT-D3. For the $\eta^1$ configurations, softening of the C-H stretching frequencies predicted by DFT vs. DFT-D3 does not exhibit a clear trend. For example, incorporating dispersion into the DFT calculations produces less softening of the C-H stretching modes for the $\eta^1$ propane and $n$-butane complexes on PdO(101), whereas two modes of the $\eta^1$ $n$-pentane complex soften to greater extent in the DFT-D3 vs. DFT calculations. The differences in vibrational frequencies determined using DFT vs. DFT-D3 reflect changes in the geometric properties and bonding of the adsorbed alkanes due to the dispersion interactions. These changes may have influence the alkane dissociation pathways and will be explored in future work.

3.4.3 Comparison of Alkane Binding on PdO(101) vs. Pd(111)

Figure 3-6 A) shows the $E_A$ vs. $N$ relations for $n$-alkanes on PdO(101) and Pd(111) estimated from experimental data and computed using DFT-D3. This plot demonstrates that the DFT-D3 calculations preserve the enhanced desorption energies of $n$-alkanes on PdO(101) vs. Pd(111), and shows that the $E_A$ vs. $N$ relations are well described by linear functions for both surfaces, in good agreement with experimental
observations. According to DFT-D3, the desorption energies of \textit{n}-alkanes on PdO(101) are \(18.0 \pm 4.4\) kJ/mol higher than on Pd(111) on average. For comparison, the experimental estimate is \(26.9 \pm 2.8\) kJ/mol.

Figure 3-6 B) shows the computed \(E_{\text{disp}}\) and \(E_{\text{elec}}\) values as a function of \(N\) for \textit{n}-alkanes adsorbed on PdO(101) and Pd(111). For methane and ethane the dispersion energies are similar in magnitude on both surfaces but the \(E_{\text{disp}}\) values on Pd(111) become larger than those on PdO(101) as the chain length increases beyond \(N = 2\). For \textit{n}-pentane, the dispersion energy is \(~11\) kJ/mol greater on Pd(111) than PdO(101). The \(E_{\text{disp}}\) vs. \(N\) relation for \textit{n}-alkanes on PdO(101) is linear with a non-zero intercept, but the slope of this relation is smaller than that of Pd(111) (10.7 vs. 14.9 kJ/mol). As a result, the alkane dispersion energies on PdO(101) fall increasingly below the dispersion energies on Pd(111) as the chain length increases. Relative to Pd(111), the lower Pd-atom density on PdO(101) produces a smaller change in the dispersion energy for each \(\text{CH}_x\) group added to the \textit{n}-alkane chain as well as a more corrugated alkane-surface dispersion interaction. Despite this difference, the dispersion energy for a given alkane differs by less than 17\% on PdO(101) compared with Pd(111) for \(N \leq 5\).

The \textit{n}-alkanes experience much stronger electronic interactions on PdO(101) compared with Pd(111). The electronic energies on PdO(101) increase from \(~16\) to 39 kJ/mol, whereas the \(E_{\text{elec}}\) values on Pd(111) increase from only -2 to 5 kJ/mol as the chain length increases from \(N = 1\) to 5. Evidence has been previously presented that \(\sigma\)-complex formation enhances the binding of \textit{n}-alkanes on PdO(101) relative to Pd(111).\textsuperscript{78, 79, 96} The present results support this conclusion as they reveal that dispersion interactions make a similar contribution to alkane binding on the two
surfaces, but that alkanes experience stronger bonding interactions on PdO(101) which raises the alkane binding energies on PdO(101) beyond those on Pd(111).

Figure 3-6. Desorption, dispersion and electronic energies vs. chain length for n-alkanes on Pd(111) and PdO(101). A) Experimental and DFT-D3 predicted desorption energies vs. chain length B) Dispersion \(E_{disp}\) and electronic \(E_{elec}\) energy vs. chain length.
3.4.4 Estimation of Dative Bond Strengths of Alkanes on PdO(101)

Rough estimates of the dative bond strengths can be obtained by evaluating electronic energy changes over the alkane chain lengths. Firstly, the strength of the alkane \( \eta^2(H, H) \) interaction on PdO(101) is estimated as equal to \( \sim 16 \text{ kJ/mol} \), which corresponds to the electronic energy of the \( \eta^2 \) CH\(_4\) complex. An estimate for the strength of one \( \eta^1(H) \) bond can be made by comparing the staggered \( \eta^1(H) \) propane (Figure 3-4 D)) with the staggered \( \eta^1(2H) \) propane configuration (Figure 3-4 A)), which shows an increase of 7.7 (10.6) kJ/mol for the DFT (DFT-D3) binding energy when going from one to two \( \eta^1(H) \) bonds. Assigning this difference in binding energy entirely to the \( \eta^1(H) \) bond is not accurate since there will be small changes to both the dispersion and other non-bonding interactions due to the shift of the propane molecule along the \textit{cus}-Pd row. To obtain a separate estimate of the \( \eta^1 \) H-Pd dative bond strength, the electronic energy changes associated with the formation of new H-Pd dative bonds as the chain length increases by consecutive CH\(_x\) groups is considered. Extending the propane chain to \( n \)-butane maintains the dative interactions at the C1 and C3 positions and introduces only weak interactions between the non-coordinated C4 methyl group and the surface. This CH\(_3\) group is directed away from the surface, and remains distant from the surface Pd and O atoms. As a result, the electronic energy increases by only 1.3 kJ/mol when the chain length increases from propane to \( n \)-butane (Figure 3-6 B)). Formation of a new H-Pd dative bond is evident in the electronic energy change (11.3 kJ/mol) that occurs in growing the chain from \( N = 4 \) to 5 (Figure 3-6 B)). In the resulting \( \eta^1 \) \( n \)-pentane complex, the C5 methyl group is directed toward the surface and one of its H-atoms is sufficiently close to a \textit{cus}-Pd atom to form a dative bond.
From these results, it is estimated that each $\eta^1$ H-Pd dative interaction between the alkanes and the PdO(101) surface is worth about 10 kJ/mol.

The strength of the $\eta^1$ H-Pd dative dative interaction is small on PdO(101) compared with binding energies reported for alkane $\sigma$-complexes of mononuclear transition metal compounds (~20 to 50 kJ/mol). However, the dative bond strength is comparable to the average dispersion energy (10.7 kJ/mol) of an alkane CH$_x$ group on PdO(101), and thus constitutes a significant portion of the CH$_x$-surface interaction energy for the CH$_x$ groups which form dative bonds. Furthermore, the dative interaction causes significant C-H mode softening and facilitates C-H bond activation. For example, it has been previously shown that H-Pd dative bonding in the $\eta^2$ CH$_4$ complex lowers the C-H bond cleavage barrier by more than 100 kJ/mol. The study demonstrates that dative bond strengths are modest for $n$-alkanes on PdO(101), but that the dative bonding has pronounced effects on C-H bond activation. Indeed, these findings underscore the importance of accurately reproducing the binding energies of alkanes on solid surfaces.

3.5 Summary

The molecular binding of $n$-alkanes on the Pd(111) and PdO(101) surfaces have been investigated using conventional DFT and the dispersion-corrected DFT-D3 method. In agreement with experimental findings, DFT-D3 predicts that $n$-alkanes bind more strongly on PdO(101) than on Pd(111), and that the desorption energies scale linearly with the alkane chain length on both surfaces. The desorption energies computed using DFT-D3, compared with conventional DFT, are in better quantitative agreement with the measured values for $n$-alkanes adsorbed on both Pd(111) and
PdO(101). DFT-D3 slightly overestimates the desorption energies of $n$-alkanes on Pd(111), with the percent differences between the computed and experimental energies ranging from 44% to 18% for CH$_4$ to $n$-C$_5$H$_{12}$. The measured desorption energies of $n$-alkanes on PdO(101) and those computed using DFT-D3 agree to within better than 2.5 kJ/mol (< 5%) for $N \leq 4$, which represents a remarkable improvement over conventional DFT.

Decomposition of the computed binding energies into dispersion and electronic components reveals that the dispersion energies are similar in magnitude for a given $n$-alkane on Pd(111) vs. PdO(101), and that dative bonding between the alkanes and cus-Pd atoms is primarily responsible for the enhanced binding of alkanes on PdO(101). By evaluating the variation of the electronic interaction energy with the alkane chain length, it is estimated that the strength of the alkane $\eta^2$(H, H) interaction on PdO(101) is ~16 kJ/mol, while a single H-Pd dative bond of an $\eta^1$ alkane complex is worth about 10 kJ/mol. Overall, this study demonstrates that the DFT-D3 method provides excellent agreement with experimentally-determined $n$-alkane desorption energies on Pd(111) and PdO(101), and may thus represent dispersion interactions with sufficient accuracy to quantitatively reproduce activation barriers for C-H bond cleavage of molecularly adsorbed alkane precursors on transitional metal and transition metal oxide surfaces.
4.1 Motivation

Alkane activation on transition metal oxides is a key step in several applications of oxidation catalysis, including the catalytic combustion of natural gas, exhaust gas remediation in automobiles, fuel cell catalysis and selective oxidation processes. Palladium oxide (PdO) is particularly interesting because this oxide is highly active in promoting the complete oxidation of alkanes. In fact, the formation of PdO is known to be responsible for the high activity of oxide-supported Pd catalysts in oxygen-rich applications of catalytic combustion. These findings provide substantial motivation for pursuing a fundamental understanding of the surface chemical properties of PdO. Indeed, PdO appears to be an exceptional case from which it may be possible to gain new insights about surface properties which tend to promote alkane activation.

Consistent with studies using supported Pd catalysts, it is found that alkane activation is facile on a PdO(101) film grown under ultrahigh vacuum (UHV) conditions, with initial C-H bond cleavage occurring below about 225 K for n-alkanes larger than ethane. The initial dissociation of alkanes on PdO(101) occurs by a precursor-mediated mechanism wherein a molecularly adsorbed state acts as the precursor for dissociation and a kinetic competition between dissociation and desorption of the precursor determines the net probability for dissociation. Through both experimental and computational studies, it has been shown that the precursor state corresponds to adsorbed alkane σ-complexes which coordinate with the PdO(101) surface by

Reprinted (adapted) from Physical Chemistry Chemical Physics, Volume 14, Issue 35, A. Antony, A. Asthagiri, J. F. Weaver. Pathways for C-H bond cleavage of propane σ-complexes on PdO(101), Pages 12202-12212. Copyright © 2012 with permission from PCCP Owner Societies and the authors.
forming dative bonds with coordinatively unsaturated (cus) Pd atoms.\textsuperscript{40, 78, 79, 96}

Recently, Kinnunen \textit{et al.} have used DFT to confirm the important role of cus-Pd atoms on PdO(101) in activating methane,\textsuperscript{107} and Hellman \textit{et al.} have reported strong evidence, based on DFT and \textit{in situ} surface X-ray diffraction, that PdO(101) is the active phase for methane oxidation over Pd(100) at ambient pressures.\textsuperscript{108} DFT calculations presented in previous chapters demonstrate that the dative bonding interactions weaken alkane C-H bonds, thereby facilitating initial C-H bond cleavage.

Recently, separate experimental studies show that propane activation on PdO(101) occurs predominantly through cleavage of primary C-H bonds.\textsuperscript{109} It is estimated that 90% of the propane molecules which react during temperature programmed (TPD) experiments do so through primary C-H bond scission. Such high selectivity for primary C-H bond activation is unusual because alkane C-H bond strengths increase in the order tertiary < secondary < primary. In accord with this trend, prior investigations show that C-H bond selectivity in alkane activation tends to follow the thermodynamically preferred route on metal surfaces, with, for example, secondary C-H bond cleavage occurring selectively over primary C-H bond cleavage in the activation of propane on Pt(110),\textsuperscript{110} Ir(111)\textsuperscript{111} and Ru(0001).\textsuperscript{112} The strong preference for primary C-H bond cleavage of propane on PdO(101) is intriguing and motivates further investigations aimed at clarifying the origin for the bond selectivity. The ability of the PdO(101) surface to coordinate relatively strongly with alkanes is an important factor in determining alkane C-H bond selectivity on this surface.

The study presented in this chapter uses DFT-D3 calculations to investigate pathways for C-H bond activation of propane complexes adsorbed on PdO(101). The
calculations predict a high selectivity toward primary C-H bond cleavage of propane on PdO(101) due to preferential population and high reactivity of propane adsorbed in an \( \eta^1 \) configuration which datively bonds to the surface through its CH\(_3\) groups. A micro-kinetic model derived from the DFT-D3 results predicts an apparent activation energy for propane dissociation on PdO(101) that agrees well with previous experimental results.

4.2 Computational Details

The calculations reported employ dispersion-corrected density functional theory (DFT-D3) that has been introduced in the previous chapter (Chapter 3). The DFT-D3 method is a combination of conventional DFT calculations implemented through the Vienna \textit{ab initio} simulation package\(^{84-86}\) and the dispersion technique (D3) developed by Grimme \textit{et al.}\(^{48,113}\) The DFT-D3 method involves computing dispersion effects separately and adding the dispersion energies and forces \((E_{\text{disp}}, F_{\text{disp}})\) to the energies and forces determined through conventional DFT electronic relaxations \((E_{\text{dft}}, F_{\text{dft}})\). The total ionic forces \((F_{\text{dft}} + F_{\text{disp}} = F_{\text{dft}} - d_3)\) are relaxed using a limited memory Broyden-Fletcher-Goldfarb-Shanno optimization method\(^{59}\) until the forces on all unconstrained atoms are less than 0.01 eV/Å. The parameters used in the DFT calculations are to the same as those used in earlier studies of the PdO(101) surface.\(^{40,79,96,114}\) Projector augmented wave (PAW) pseudo potentials\(^{89}\) provided in the VASP database are used along with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional\(^{33}\) and a plane wave cutoff of 400 eV. Energy calculations to determine \(E_{\text{dft}}\) are done using the residual minimization method with direct inversion in the iterative subspace for electronic relaxations accelerated using Methfessel-Paxton Fermi-level smearing\(^{101}\) with
a Gaussian width of 0.1 eV. The dispersion energy \( E_{\text{disp}} \) used in the DFT-D3 formulation is given by Equation 4-1, where the pairwise interactions are summed over all the atoms within a cutoff radii of 50 Å. \( E_{\text{disp}} \) is a function of \( n \)th order inter-nuclear distances \( r_{AB}^{-n} \), dispersion coefficients \( C_n^{AB} \) that have been computed \textit{ab initio} by time-dependent DFT, a scaling fraction \( s_n \) that ensures asymptotic exactness and a damping function \( f_{d,n}(r) \). The parameters have been directly taken from the most recent implementation of dispersion in DFT calculations by Grimme \textit{et al.}\textsuperscript{48}

\[
E_{\text{disp}} = -\frac{1}{2} \sum_{AB} \left[ s_6 \frac{C_6^{AB}}{r_{6}^{AB}} f_{d,6}(r_{AB}) + s_8 \frac{C_8^{AB}}{r_{8}^{AB}} f_{d,8}(r_{AB}) \right] \quad (4-1)
\]

DFT-D3 study of the adsorption of \( n \)-alkanes on PdO(101) described in chapter 3 show that DFT-D3 adsorption energies are within 2.5 kJ/mol (< 5%) of the experimental-derived values for alkane chain lengths up to \( n \)-butane.\textsuperscript{40}

The PdO(101) thin film used in experimental studies are grown on a Pd(111) substrate at 500 K by oxidizing the metal surface in UHV using an oxygen atom beam. The generated film is \( \sim 13 \) Å thick and consists of \( \sim 3 \) ML of oxygen atoms, where 1 ML is defined equivalent to the Pd(111) surface atom density of \( 1.53 \times 10^{15} \) cm\(^{-2} \). Figure 4-1 depicts the stoichiometric PdO(101) surface comprising of alternating rows of coordinatively unsaturated \((\text{cus})/\)threefold \((3f)\) and coordinatively saturated \((\text{cs})/\)fourfold \((4f)\) Pd and O atoms. The side view of PdO(101) shows that the coordinative environment associated with each \textit{cus}-Pd atom resembles a square planar Pd complex with a coordination vacancy directed away from the surface and three oxygen ligands, one of which is a \textit{cus}-O atom. The \textit{cus} sites being unsaturated are found to be highly active in all the previous studies employing different molecular species.\textsuperscript{83, 88, 94, 114, 115}
The 1.4 ML of atoms on the PdO(101) surface are equally distributed as *cus* and 4f-Pd and O atom resulting in 0.35 ML of *cus*-Pd sites on the surface.

The computational model of the PdO(101) surface is derived by slicing bulk crystalline PdO along the (101) plane, followed by straining the model to match the lattice parameters reported by low energy electron diffraction experiments ($a = 3.057 \text{ Å}, b = 6.352 \text{ Å}$). The bulk terminated PdO(101) surface is defined by a rectangular unit cell where the $\vec{a}$ and $\vec{b}$ lattice vectors correspond to [010] and [10̅1] directions of the PdO crystal, respectively (Figure 4-1).

![Figure 4-1](image.png)

Figure 4-1. Stoichiometric PdO(101) surface. Comprises of 0.35 ML of *cus*-Pd, *cus*-O, 4f-Pd and 4f-O each. $\vec{a}$ and $\vec{b}$ represent the [010] and [10̅1] crystallographic directions. The *cus*-Pd atoms aligned along the $\vec{a}$ direction collectively form the *cus*-Pd row.

The strained model is relaxed after fixing the bottom layer for stability. The computational model of the PdO(101) surface used in the studies consists of four layers.
totaling a thickness of ~9 Å and omits the Pd(111) metal substrate. Previous studies show that a thickness of 9 Å is sufficient to ignore the metal substrate as increasing the layer thickness does not affect the interaction between the chemisorbing species and the surface. The supercell has a vacuum spacing of ~20 Å normal to the surface in order to eliminate spurious periodic interactions in this direction. A $2 \times 4 \times 1$ ($4 \times 2 \times 1$) Monkhorst-Pack $k$-point mesh has been used for the $2 \times 2$ ($4 \times 1$) unit cell sizes, respectively. The $2 \times 2$ ($4 \times 1$) unit cell sizes are derived by doubling the unit cell size along $\bar{a}$ and $\bar{b}$ (quadrupling the unit cell size along $\bar{a}$ alone). The $2 \times 2$ and $4 \times 1$ unit cells are used to investigate propane binding configurations along the $\bar{b}$ and $\bar{a}$ directions, respectively.

The adsorption/binding energies reported in this study ($E$) are defined as the difference between the sum of total energies (electronic plus dispersion, $E_{dft-d3}$) for the isolated molecule ($E_{iso}$) and bare surface ($E_{bare}$) with that of the chemisorbed molecule/surface system ($E_{chemisorb}$) as represented in Equation 4-2.

$$E = [E_{bare} + E_{iso}] - E_{chemisorb}$$

(4-2)

Note that the “electronic” energy of the adsorbate system is specified as the difference between the total binding energy determined for a relaxed structure using the DFT-D3 method and the dispersion energy. To determine the electronic energy, a single-point calculation is performed using conventional DFT, i.e., without the dispersion correction, for a relaxed structure found using DFT-D3. These calculations enables quantifying the energetic contributions of dispersion interactions separately from the contributions made by other bonding interactions. Propane binding energies are reported based on a single
propane molecule (kJ/mol C₃H₈) chemisorbed on a 2 × 2 or 4 × 1 PdO(101) supercell for which the coverage is equal to 0.0875 ML. The simulated coverage is close to experimental estimates of the saturation coverage (~0.09 ML). The propane σ-complexes in the supercells are separated by more than 6 Å at 0.0875 ML and interact only weakly with one another. The various propane configurations determined on the surface are confirmed to be true minima by performing normal mode analyses, where the frequencies of the vibrational modes are calculated by fixing the surface atoms while leaving the propane molecule unconstrained. The computed vibrational frequencies are used to calculate zero-point corrections for the total energies. Propane activation pathways were investigated using the climbing nudged elastic band (NEB) method, and normal mode analyses were performed on the transition states to confirm the presence of a single imaginary frequency. In all geometrical optimizations and NEB calculations, the bottom layer of the PdO(101) slab is fixed in order to retain the bulk structure while all other degrees of freedom of the solid and the propane molecule are allowed to fully relax. Vibrational frequencies computed for the different states are employed to determine desorption and reaction rate constants used in the micro-kinetic model which is described in detail in a subsequent section.

4.3 Results and Discussion

4.3.1 Molecular Chemisorption of Propane on PdO(101)

Several configurations were identified for adsorbed propane σ-complexes on the PdO(101) surface, each of which could serve as an initial state for C-H bond activation. Some details of the propane complexes are given in chapter 2.⁴⁰ Here, a more comprehensive information about the adsorption of propane on PdO(101) is presented.
Propane can adsorb in both $\eta^2$ and $\eta^1$ binding configurations on PdO(101). An $\eta^2$ configuration results from a three-center interaction in which a CH$_2$ or CH$_3$ group resides on top of a cus-Pd atom and two H-atoms of the CH$_n$ group coordinate with the cus-Pd atom. The plane containing the H-C-H bond angle of the Pd-coordinated H-atoms aligns parallel to the cus-Pd row, thus causing the molecular plane to align perpendicularly to the cus-Pd row. Propane can also bind in $\eta^1$ configurations in which the molecule aligns parallel to the cus-Pd row and single H-Pd dative bonds form at different cus-Pd atoms.

Figure 4-2 shows representations of the stable binding configurations of propane $\sigma$-complexes adsorbed on PdO(101) that we predict using DFT-D3. Table 4-1 lists the corresponding binding energies and the contributions from dispersion and electronic energies to the total binding energies. These configurations are named based on (i) the type of CH$_n$ group involved in the dative interaction with a cus-Pd atom (‘p’-primary or ‘s’-secondary), (ii) the number of dative interactions, (iii) the type of interactions (‘$\eta^2$’ or ‘$\eta^1$’)) and (iv) other geometrical features of the configuration (‘+$/-$’ towards/away from the cus-O atoms; ‘st’-staggered vs. ‘fl’-flat lying geometry). Calculations predict that propane can adopt a stable $\eta^2$ configuration on PdO(101) by binding through the CH$_2$ group (s-$\eta^2$) and can also adopt two $\eta^2$ configurations by binding through a CH$_3$ group with the molecule leaning either towards or away from the cus-O atoms (p-$\eta^2(+)\text{ and p}-\eta^2(-)$).

Also, propane can adsorb in η^1 configurations in which the CH_2 group forms a single H-Pd dative bond (s-η^1) or each CH_3 group forms a single H-Pd dative bond at different Pd-atoms resulting in two H-Pd dative bonds per molecule (p-2η^1). Further, the η^1 configurations can adopt distinct geometries in which the molecular plane aligns close to the surface normal (“st-staggered”) or leans toward the adjacent 4f-Pd row (“fl-flat-lying”).
Table 4-1. Dispersion, electronic, binding and zero-point corrected binding energies of different propane configurations on the PdO(101) surface. The zero-point corrections treat all 3N modes of motion of the adsorbed structures as harmonic vibrations. The binding energy is equal to the sum of the dispersion and the electronic energy as described in the Computational Details section.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Dispersion Energy</th>
<th>Electronic Energy</th>
<th>Binding Energy (E)</th>
<th>E(ZPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-η²(+)</td>
<td>42.1</td>
<td>17.1</td>
<td>59.1</td>
<td>58.9</td>
</tr>
<tr>
<td>s- η²</td>
<td>44.7</td>
<td>24.4</td>
<td>69.1</td>
<td>69.5</td>
</tr>
<tr>
<td>p-η²(-)</td>
<td>42.2</td>
<td>15.1</td>
<td>57.3</td>
<td>57.0</td>
</tr>
<tr>
<td>p-2η¹(st)</td>
<td>47.1</td>
<td>24.8</td>
<td>72.0</td>
<td>70.5</td>
</tr>
<tr>
<td>p-2η¹(fl)</td>
<td>47.1</td>
<td>23.4</td>
<td>70.5</td>
<td>67.5</td>
</tr>
<tr>
<td>s-η¹(st)</td>
<td>45.0</td>
<td>17.0</td>
<td>62.0</td>
<td>63.1</td>
</tr>
<tr>
<td>s-η¹(fl)</td>
<td>45.6</td>
<td>18.3</td>
<td>64.0</td>
<td>66.1</td>
</tr>
</tbody>
</table>

* Energies are reported in kJ/mol C₃H₈

The p-2η¹(st) configuration is the most stable configuration among the propane σ-complexes on PdO(101), and has a zero-point corrected binding energy of 70.5 kJ/mol.⁴⁰ The s-η² and p-2η¹(fl) configurations lie close in energy to the preferred p-2η¹(st) configuration, with ZPC binding energies of 69.5 and 67.5 kJ/mol, respectively. The s-η¹ complexes form only one H-Pd dative bond per molecule and are thus less stable than the p-2η¹ complexes. The extra H-Pd dative bond of the p-2η¹ complexes causes the electronic energies to be about 7 kJ/mol higher for the p-2η¹ vs. s-η¹ complexes, whereas the dispersion energies are within about 2 kJ/mol among all of the η¹ complexes (Table 4-1). Differences in zero-point vibrational energies bring the binding energies of the s-η¹ complexes closer to those of the p-2η¹ complexes than is indicated by the electronic and dispersion energies alone. In particular, DFT predicts that the zero-point vibrational energy decreases when propane adsorbs into an s-η¹ configuration, but increases upon formation of a p-2η¹ complex. The reason for this difference is that the constrained molecular geometry of the p-2η¹ configuration causes
many of the low frequency modes (< 1500 cm\(^{-1}\)) to stiffen relative to those of the isolated molecule. The net effect is that the most stable s-\(\eta^1\) and p-2\(\eta^1\) complexes differ in ZPC binding energy by only 4.4 kJ/mol (Table 4-1).

Comparison of the electronic energies (Table 4-1) suggests that a single H-Pd \(\eta^1\) dative bond is stronger when the dative bonding occurs through a secondary vs. a primary H-atom of the propane molecule. As a rough approximation, one may consider that the entire electronic energy of the s-\(\eta^1\) complexes is equal to the strength of a secondary H-Pd dative bond, while one half of the electronic energy of the p-2\(\eta^1\) complexes is equal to the primary H-Pd dative bond strength in these complexes. Such a comparison suggests that the secondary H-Pd dative bonds in the s-\(\eta^1\) complexes are about 6.5 kJ/mol more stable than primary H-Pd dative bonds in the p-2\(\eta^1\) complexes. Differences in molecule-surface Coulombic interactions could also account for a substantial portion of the electronic energy differences among the s-\(\eta^1\) and p-2\(\eta^1\) configurations. However, DFT also predicts that the Pd-coordinated C-H bond experiences greater mode softening and elongation in the s-\(\eta^1\) complexes compared with the p-2\(\eta^1\) complexes as well as greater accumulation of charge in the H-Pd dative bond. For example, the asymmetric stretching vibration associated with the Pd-coordinated CH\(_2\) group red-shifts by 415 cm\(^{-1}\) upon formation of the s-\(\eta^1\)(st) complex, while an asymmetric stretching vibration for each CH\(_3\) group red-shifts by about 200 cm\(^{-1}\) for the p-2\(\eta^1\)(st) complex. These characteristics suggest that secondary H-Pd dative bonds are slightly stronger than primary H-Pd dative bonds in the \(\eta^1\) propane complexes, and that the Pd-coordinated, secondary C-H bonds are weaker as a result. Despite this difference between Pd-coordinated primary and secondary C-H bonds,
DFT-D3 predicts lower energy barriers for primary vs. secondary C-H bond cleavage of the p-2η¹ vs. s-η¹ complexes, thus indicating that C-H bond softening in the initial state, while important, is not the decisive factor in determining the relative energy barriers for primary vs. secondary C-H bond cleavage of propane σ-complexes on PdO(101).

Lastly, the p-η² complexes are the least stable adsorbed propane σ-complexes that have identified on PdO(101), with ZPC binding energies near 58 kJ/mol. The low stability of the p-η² complexes arises from unfavorable Coulombic interactions between the propane molecule and the surface atoms. For example, the electronic energy of the p-η²(-) complex is 9.4 kJ/mol lower than that of the s-η² complex, while the dispersion energy is lower by only 2.5 kJ/mol. The population of p-η² propane complexes on PdO(101) is likely to be negligibly small compared with the other complexes due to the weaker binding in that state. In contrast, the ZPC binding energies of the p-2η¹(st), p-2η¹(fl), s-η¹(fl) and s-η² complexes span an energy range of less than 4.5 kJ/mol, which suggests that propane molecules could attain appreciable populations in each of these configurations, particularly if entropic factors offset differences in binding energy. For this reason, C-H bond activation from each of these molecular states must be considered in evaluating the overall reactivity of propane on PdO(101).

It is worth noting that propane desorption from PdO(101) produces broad TPD features, which is consistent with the co-existence of several configurations of the adsorbed propane molecules. However, direct experimental evidence of the specific configurations that are predicted by DFT is not yet available. Using surface vibrational spectroscopy, it may be possible to distinguish and characterize propane adsorbed in different configurations on PdO(101), particularly for configurations in
which propane bonds to the surface through the primary vs. secondary C-H bonds. While such data is not yet available, a very good agreement is observed between DFT calculations and experimental measurements of the reactivity of propane on PdO(101), including accurate reproduction of the high selectivity toward primary C-H bond activation.\textsuperscript{109} This agreement lends confidence to the validity of the molecular structures and reaction pathways identified using DFT.

4.3.2 Pathways for Propane Activation on PdO(101)

The C-H bond cleavage pathways for each of the propane complexes identified on the PdO(101) surface is investigated. Since previous work reveals that coordination with the Pd center lowers the energy barriers for C-H bond cleavage significantly,\textsuperscript{96} we focused on determining pathways in which only the Pd-coordinated C-H bonds undergo activation. In a prior study of methane activation on PdO(101), a pathway for C-H bond scission of an adsorbed CH\textsubscript{4} \(\eta^2\) complex in which one of the Pd-coordinated C-H bonds is broken is identified.\textsuperscript{96} In this pathway, the CH\textsubscript{4} molecule rotates about the \textit{cus}-Pd atom and transfers one of the Pd-coordinated H-atoms to the neighboring \textit{cus}-O atom, thus producing an HO group and a CH\textsubscript{3}-Pd moiety. While the CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8} \(\eta^2\) complexes adopt analogous binding geometries at the \textit{cus}-Pd site, it is found that steric repulsions with adjacent surface atoms prevent the propane \(\eta^2\) complexes from rotating into a configuration that leads to C-H bond cleavage. In particular, the remote portions of the s-\(\eta^2\) and p-\(\eta^2\)(+) complexes interact repulsively with the \textit{cus}-O row as the molecule tries to position itself for H-atom transfer, while the p-\(\eta^2\)(-) complex is repelled by the 4f-Pd facet during the rotation. These steric repulsions effectively prevent the propane \(\eta^2\) complexes from directly undergoing C-H bond cleavage. Rather than
causing dissociation, molecular rotation about the CH$_n$-Pd dative bond initiates configurational changes from $\eta^2$ to $\eta^1$ geometries. The calculations predict that propane can readily convert from the $\eta^2$ to $\eta^1$ configurations. For example, only the thermochemical barrier must be overcome in the conversion of the s-$\eta^2$ complex to a s-$\eta^1$ complex, and the conversion from p-$\eta^2$ to p-$2\eta^1$ complexes is exothermic and barrierless. Thus, while C-H bond activation of the propane $\eta^2$ complexes is sterically hindered, the $\eta^2$ complexes can readily transform to the $\eta^1$ configurations.

Figure 4-3. The initial (IS), transition (TS) and final (FS) states corresponding to C-H bond cleavage of $\eta^1$ propane configuration on PdO(101). A) p-2$\eta^1$(st). B) p-$2\eta^1$(fl). C) s-$\eta^1$(st). D) s-$\eta^1$(fl).

Facile C-H bond activation pathways are predicted for each of the propane $\eta^1$ complexes identified on PdO(101). Figure 4-3 shows representations of the molecular structures for each initial state (IS), transition state (TS) and final state (FS) for the reaction pathways that were determined. In each case, the adsorbed propane complex transfers one of the Pd-coordinated H-atoms to a neighboring cus-O atom to afford an
OH group and a propyl-Pd moiety. For each p-2\(\eta^1\) complex, motion on the reaction pathway preserves the H-Pd dative bond at the non-reacting CH\(_3\) group as the other CH\(_3\) group moves toward a \textit{cus}-O atom to transfer a H-atom. For example, the propane p-2\(\eta^1\)(st) complex brings a CH\(_3\) group close to the \textit{cus}-O atom by rotating about the H-Pd dative bond of the non-reacting CH\(_3\) group. After H-atom transfer, the 1-propyl fragment moves into a nearly parallel orientation along the \textit{cus}-Pd row, and maintains the H-Pd dative bond at the remaining CH\(_3\) group. For each s-\(\eta^1\) complex, the molecules translate toward the \textit{cus}-O atom row to transfer the Pd-coordinated secondary H-atom. The resulting 2-propyl fragments then adopt flat-lying configurations along the \textit{cus}-Pd row.

The DFT-D3 calculations predict that primary C-H bond cleavage is energetically favored over secondary C-H bond cleavage in the activation of propane on PdO(101). Table 4-2 lists the ZPC energy for each IS, TS and FS as well as the energy barriers for C-H bond cleavage relative to the appropriate molecularly adsorbed state. Figure 4-4 summarizes this information in the form of an energy diagram for propane adsorption and activation on PdO(101). In Table 4-2, the symbols \(\Delta E_{d,i}^\pi\) and \(\Delta E_{r,i}^\pi\) represent the energy barriers for desorption and energy barrier for reaction \textit{via} C-H bond cleavage of IS \(i\). The quantity \(E_{\text{app}} = \Delta E_{r,i}^\pi - \Delta E_{d,i}^\pi\) is the apparent energy barrier for reaction, which is the reaction barrier measured relative to the energy of a gas-phase propane molecule. From these definitions, it may be seen that \(\Delta E_{d,i}^\pi\) and \(\Delta E_{d,i}^\pi - \Delta E_{r,i}^\pi\) are equal to the binding energies of IS and TS \(i\), respectively.
Table 4-2. Zero-point corrected binding energies (3N vibrational modes) of different states evolving from the activation of primary and secondary bound $\eta^1$ propane configurations on PdO(101) surface along with energy barrier for C-H bond cleavage. The binding energy, prior to zero-point corrections, is equal to the sum of the dispersion and the electronic energy as described in the Computational Details section.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Initial State ($\Delta E_{d,i}^\pm$)</th>
<th>Transition State ($\Delta E_{d,i}^\pm - \Delta E_{r,i}^\pm$)</th>
<th>Final State ($E_{FS}$)</th>
<th>Reaction Barrier ($\Delta E_{r,i}^\pm$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-$2\eta^1$(st)</td>
<td>70.5</td>
<td>18.7</td>
<td>112.2</td>
<td>51.8</td>
</tr>
<tr>
<td>p-$2\eta^1$(fl)</td>
<td>67.5</td>
<td>14.7</td>
<td>111.2</td>
<td>52.8</td>
</tr>
<tr>
<td>s-$\eta^1$(st)</td>
<td>63.1</td>
<td>9.0</td>
<td>112.6</td>
<td>54.1</td>
</tr>
<tr>
<td>s-$\eta^1$(fl)</td>
<td>66.1</td>
<td>5.1</td>
<td>104.5</td>
<td>61.0</td>
</tr>
</tbody>
</table>

* Energies are reported in kJ/mol C$_3$H$_8$

The DFT-D3 calculations predict that the apparent energy barrier for reaction is negative for each $\eta^1$ propane complex, i.e., the TS energy levels lie below the gas-phase zero (Figure 4-4), which means that C-H bond cleavage is energetically preferred over molecular desorption. Indeed, activation of the most stable initial state, the p-$2\eta^1$(st) propane complex, is the energetically preferred pathway for C-H bond cleavage among all of the propane complexes on PdO(101). DFT-D3 predicts that the intrinsic energy barrier for C-H bond cleavage of the p-$2\eta^1$(st) complex is 51.8 kJ/mol, which is slightly lower than the predicted energy barriers of 52.8 and 54.1 kJ/mol for C-H bond cleavage of the p-$2\eta^1$(fl) and s-$\eta^1$(st) complexes, respectively. The higher reaction barrier for the s-$\eta^1$(fl) complex ($\Delta E_{r,i}^\pm = 61.0$ kJ/mol) correlates with the lower relative stability of the 2-propyl final state in this case. For the favored dissociation pathways, the calculations predict that the intrinsic barrier for primary C-H bond cleavage is lower by 2.3 kJ/mol than the barrier for secondary C-H bond cleavage. The DFT-D3 results are consistent with experimental finding of a strong preference for primary C-H bond activation of propane on PdO(101).$^{109}$
Figure 4-4. Energy diagram for initial C-H bond cleavage pathways of propane \( \eta^1 \) configurations on PdO(101). A) \( p-2 \eta^1(st) \). B) \( p-2 \eta^1(fl) \). C) \( s-\eta^1(st) \). D) \( s-\eta^1(fl) \). The diagram shows the ZPC energy levels of the IS, TS and FS for each propane complex, with the isolated propane molecule taken as the zero of energy.
The calculations suggest that two factors give rise to the high selectivity for primary C-H bond activation of propane on PdO(101). The first is that propane binds more strongly to the surface in the p-2η¹ configuration than in the s-η¹ configuration, and will thus preferentially adsorb into a configuration in which only primary C-H bonds coordinate strongly with the surface. In addition, the intrinsic energy barriers for C-H bond cleavage are lower for the p-2η¹ complexes compared with the s-η¹ complexes. The combination of these two effects is evident in the apparent energy barriers for reaction of the p-2η¹ vs. s-η¹ complexes; for example, $E_{\text{app}}$ for the p-2η¹(st) complex is nearly 10 kJ/mol lower than that of the s-η¹(st) complex (Table 4-2). The lower value of $E_{\text{app}}$ demonstrates that the TS for activation of the p-2η¹(st) complex is more stable than that of the s-η¹ complex. This stability arises largely from the extra H-Pd dative bond that is maintained during activation of the p-2η¹(st) complex (Figure 4-3) and is proportional to the difference in binding in the initial states. Since the intrinsic reaction barrier is also lower for the p-2η¹(st) complex, effects other than the extra H-Pd dative bond must also act to stabilize the TS for primary vs. secondary C-H bond activation.

4.3.3 Charge Distribution within the Propyl Transition Structures

Analysis of the atomic charges of the TSs reveals that propane C-H bond cleavage on PdO(101) is heterolytic and that the 1-propyl TS adopts a more stabilizing charge distribution than the 2-propyl TS. Figure 4-5 illustrates group charges of the propane molecule at the initial and transition states for C-H bond activation of the p-2η¹ vs. s-η¹ complexes, where the charges for each CH₃ group are obtained by summing atomic charges as determined using the density derived electrostatic and chemical (DDEC) charge analysis reported by Manz and Sholl. The charge analysis shows that
the propane complexes are positively charged by about $+0.15e$, with most of the positive charge localized on the CH$_2$ group. The positive charge of the propane molecules demonstrates that $\sigma$-complex formation involves net donation of electrons to the surface. The analysis further reveals that the transferred H-atom has a partial positive charge of $+0.21e$ and $+0.24e$ at the TSs for primary and secondary C-H bond activation, respectively. At each TS, the total charge of the propyl group is nearly zero but charge is more polarized within the 1-propyl group.

As seen in Figure 4-5, the activated CH$_2$ group of the 1-propyl TS has a net charge of $-0.19e$ while the neighboring CH$_2$ group has a charge of $+0.18e$, giving a charge difference of $0.37e$. In contrast, the charge difference is only $0.09e$ between the activated CH group and each CH$_3$ group of the 2-propyl TS. To check that $1^\circ$ C-H bond
activation produces the more stabilizing charge distribution, the change in Coulomb energy of the propyl substituent for each reaction pathway is calculated, the atomic charges are used to obtain an approximation of the Coulomb energy. The charge of the transferred H-atom is excluded to compare how the charge distribution within the 1- vs. 2-propyl “substituents” change during C-H bond cleavage. These calculations reveal that the Coulomb energy of the 1-propyl species becomes more stabilizing when the p-2\(\eta^1\) species accesses the TS, while the Coulomb energy of the 2-propyl group increases (i.e., becomes less stabilizing) as the s-\(\eta^1\) complex dissociates.

The higher stability of the 1-propyl vs. 2-propyl TS on PdO(101) is consistent with reports of the relative stabilities of propyl anions in the gas-phase. Other researchers report that the proton affinity of the 1-propyl anion is lower than that of the 2-propyl anion by about 16 kJ/mol.\(^{116,117}\) For comparison, the homolytic bond dissociation energy of a primary C-H bond of an alkane is about 12 kJ/mol higher than that of a secondary C-H bond. The relative stabilities of alkyl anions are thought to be determined by the ease with which the substituents of these species can be polarized and thus develop a group dipole that stabilizes the negative C center of the anion, i.e., substituent polarization. The larger \(\text{C}_2\text{H}_5\) substituent of the 1-propyl anion should be able to adopt a more stabilizing charge distribution than the CH\(_3\) groups of the 2-propyl anion, thus yielding a lower proton affinity for the 1- vs. 2-propyl anion. The distribution of charge found within the 1-propyl and 2-propyl TSs on PdO(101) are qualitatively consistent with the behavior expected for the gas-phase propyl anions. A key implication is that the development of a more stabilizing charge distribution within the 1-propyl TS acts to lower the energy barrier for C-H bond cleavage, and thus makes the intrinsic energy
barrier for primary C-H bond cleavage lower than that for secondary C-H bond cleavage.

4.3.4 Micro-kinetic Modeling of Propane C-H Bond Activation on PdO(101)

A micro-kinetic model is developed to simulate the kinetics governing the initial C-H bond activation and selectivity of propane on PdO(101), with kinetic parameters derived from the DFT-D3 structures. Key goals of the simulations are to evaluate the kinetic competition among various reaction pathways and predict kinetic information that is comparable with data obtained in previous experiments. The model is most appropriate for reaction at low propane coverage since intermolecular interactions among adsorbates are not taken into account. In the model, it is considered that propane can adsorb into any of the four \( \eta^1 \) configurations or the s-\( \eta^2 \) configuration and that the resulting molecular species can either desorb or react. The p-\( \eta^2 \) states are omitted from the model since the relatively weak binding causes the concentrations of molecules in these states to be negligibly low. The model also assumes that the molecular complexes exist in a quasi-equilibrium such that the relative populations among these states are well-approximated by an equilibrium distribution. The rationale for the quasi-equilibrium assumption is the finding that transitions from one molecular configuration to another occur with small barriers relative to the energy barriers for desorption and C-H bond cleavage. As mentioned above, it is found that only the thermochemical barriers are to be overcome for the conversion of the s-\( \eta^2 \) to s-\( \eta^1 \) configurations and p-\( \eta^2 \) to p-2\( \eta^1 \) configurations. Similarly, barriers of only \(~8\text{ kJ/mol}\) control interconversion between the \( \eta^1(\text{fl}) \) and \( \eta^1(\text{st}) \) configurations. Although pathways for conversion between the primary-bonded and secondary-bonded complexes (e.g., s-
η^1 to p-2η^1, etc.) have not been explored, it is reasonable to expect that such processes occur more rapidly than desorption or C-H bond scission.

The steps included in the kinetic model may be represented by the following equations,

Desorption from state \( i \)
\[ \text{RH}(i) \rightarrow \text{RH(gas)} \quad [k_{d,i}] \]

Reaction from state \( i \) (initial C-H bond cleavage)
\[ \text{RH}(i) \rightarrow R(i) + H \quad [k_{r,i}] \]

Conversion between molecular states
\[ \text{RH}(i) \rightleftharpoons \text{RH}(j) \]

The symbols \( k_{d,i} \) and \( k_{r,i} \) represent the desorption and reaction rate coefficients for molecular state \( i \), respectively, and it is assumed that inter conversion among the molecular states is rapid such that the molecular species reach a quasi-equilibrium. Under the equilibrium assumption, the mole fraction in molecular state \( i \) is given by the equation,

\[ y_i = \frac{K_i}{\sum K_i} \quad (4-3) \]

where \( K_i \) represents the adsorption equilibrium constant for state \( i \). The desorption and reaction rate coefficients for each molecular state are calculated using the following equations derived from transition state theory (TST),

\[ k_{d,i}(T) = l_{d,i} \frac{k_B T}{h} \frac{q_i^{2D} q_{vib(g)}}{q_{ad,i}} e^{-\Delta E_{d,i}^\neq/RT} \quad (4-4) \]

\[ k_{r,i}(T) = l_{r,i} \frac{k_B T}{h} \frac{q_i^\neq}{q_{ad,i}} e^{-\Delta E_{r,i}^\neq/RT} \quad (4-5) \]

In these equations, \( \Delta E_{d,i}^\neq \) and \( \Delta E_{r,i}^\neq \) represent the ZPC energy barriers for desorption and reaction of molecular state \( i \), respectively, the quantities \( q_i^{2D} \) and \( q_r \) represent
partition functions for two-dimensional (2D) translation and three-dimensional (3D) rotation of a gas-phase molecule, \( q_{\text{vib}(g)} \) represents the vibrational partition function of a gas-phase propane molecule and \( q_{\text{ad},i} \) and \( q_{i}^{\neq} \) represent the partition functions for adsorbed state \( i \) and the dissociation transition state for configuration \( i \), respectively. The symbols \( l_{d,i} \) and \( l_{r,i} \) represent statistical factors\(^{118} \) for the desorption and reaction of molecular state \( i \) where the statistical factors correspond to the number of equivalent pathways leading from an IS to a TS. The statistical factors are equal to two for reaction of the p-2\( \eta^1 \) complexes, and unity for all other pathways. The translational partition function is evaluated for two degrees of freedom because the transition state for desorption is taken as the gas-phase molecule less translational motion perpendicular to the surface. The 2D translational and 3D rotational partition functions of a gas-phase propane molecule are calculated using the following equations,

\[
q^{2D}_t = \frac{2\pi mkTA}{h^2} \tag{4-6}
\]

\[
q_r = \pi^{1/2} (I_x I_y I_z)^{1/2} \left( \frac{8\pi^2 kT}{h^2} \right)^{3/2} \tag{4-7}
\]

The quantities \( m \) and \( I_j \) represent the mass of the propane molecule and the moment of inertia for rotation about principal axis \( j \) of the molecule, respectively. The principal moments of inertia of propane are given by Tait et al.\(^{106} \) Note that the symmetry number of propane is omitted from Equation 4-7 because statistical factors are used instead.\(^{118} \)

The quantity \( A \) represents the area occupied by a propane molecule when the PdO(101) surface is saturated with propane \( \sigma \)-complexes. For the calculations, the saturation coverage is taken to be 0.0875 ML, which is equal to one fourth of the \textit{cus}-Pd
atom density. The value estimated from experimental data is ~0.09 ML. The formula for a set of uncoupled harmonic oscillators is used to evaluate vibrational partition functions for a gas-phase molecule and adsorbed states, with the vibrational frequencies determined from normal mode analysis of the DFT-derived structures. The equations used to calculate the adsorption equilibrium constants are analogous to the expression for the desorption rate coefficient (Equation 4-4).

Rate coefficients are calculated using two descriptions of the partition functions for the adsorbates and dissociation transition states. In one description, it is assumed that all modes of motion for the adsorbed species are harmonic vibrations and thus set the partition functions for the adsorbed states equal to those for a set of $3N$ harmonic oscillators as given by the following equation,

$$q_{ad,i} = q_{vib,i} = \prod_{j=1}^{3N} \left( 1 - \exp \left( \frac{-\hbar \nu_j}{k_B T} \right) \right)^{-1}$$

(4-8)

where $\nu_j$ represents the frequency of normal mode $j$ and the product is evaluated over all $3N$ normal modes of the adsorbed state. The equation for $q_{vib}^j$ is similar but involves only the $3N-1$ real vibrational modes of the transition structures for C-H bond cleavage. Several of the frustrated adsorbate motions are characterized by low frequencies ($< 150$ cm$^{-1}$), and are thus likely to exhibit relatively unhindered motion at the temperatures of interest. In this case, one can expect that the $3N$ harmonic oscillator model would underestimate the entropy associated with the adsorbed structures. These considerations motivated application of an alternate description of the adsorbate partition functions in which two of the frustrated motions of the adsorbed species are treated as free motions while the remaining $3N-2$ modes as harmonic vibrations. It is
emphasized that this approach is approximate since other modes may also deviate from
the harmonic model and the frustrated adsorbate motions are not truly free motions. A
key goal of conducting the $3N-2$ model calculations is to assess the sensitivity of the
kinetic pre-factors to the approach used for describing the states of the weakly-hindered
adsorbate motions. Obtaining a more accurate description of the frustrated motions lies
outside of the scope of the present work. Another objective was to determine if the $3N-2$
model provides a more accurate representation of experimentally-determined
dissociation probabilities of propane on PdO(101) compared with the $3N$ model.

In the $3N-2$ model, it is assumed that the adsorbed species execute free
translation in one dimension, along the $cus$-Pd row, as well as free rotation about a
single axis. For the $\eta^1$ complexes, it is assumed that rotation occurs freely about the $C_{1v}$
axis contained within the C-C-C plane, which promotes transitions between the
staggered and flat-lying configurations. For the $s-\eta^2$ complex, it is assumed that free
rotation occurs about the $C_{2v}$ axis of the propane molecule. It is also assumed that the
free motions are maintained in the transition state for dissociation. Under these
assumptions, the partition functions for the adsorbed complexes are computed using
the following equations,

$$q_{aa} = q_t^{1D} q_r^{1D} q_v^{3N-2} \quad (4-9)$$

where,

$$q_t^{1D} = \left( \frac{2\pi m k T A}{\hbar^2} \right)^{1/2} \quad (4-10)$$
and

\[ q_{r}^{1D} = \left( \frac{8\pi^2 I k T}{\hbar^2} \right)^{1/2} \]  

(4-11)

In these equations, \( q_{t}^{1D} \) and \( q_{r}^{1D} \) represent partition functions for free translation and rotation in one dimension,\(^{119}\) respectively, and \( q_{vib}^{3N-2} \) represents the partition function obtained when the remaining \( 3N - 2 \) modes of motion are treated as harmonic oscillators. The moment of inertia \( I \) for an adsorbed complex is taken to be equal to a principal moment of inertia of a gas-phase propane molecule for rotation about either the \( C_{1v} \) or \( C_{2v} \) molecular axis. To compute the partition function for 1D translation, the characteristic length scale per molecule is defined as the area occupied by an adsorbed propane complex at 0.0875 ML raised to the one half power.

Table 4-3 lists average values of the kinetic pre-factors for desorption (\( \nu_d \)) and reaction (\( \nu_r \)) computed using the \( 3N \) and \( 3N - 2 \) models. The table shows average values of the pre-factors for the temperature range from 150 to 350 K. The desorption pre-factors obtained from the \( 3N \) model range from \( \log(\nu_d) = 16.4 \) to 17.5, which lies within the range expected for a free vs. fully constrained propane adsorbate.\(^{106}\)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( 3N ) model</th>
<th>( 3N - 2 ) model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \log(\nu_d) )</td>
<td>( \log(\nu_r) )</td>
</tr>
<tr>
<td>p-2( \eta^1(\text{st}) )</td>
<td>17.5</td>
<td>11.6</td>
</tr>
<tr>
<td>p-2( \eta^1(\text{fl}) )</td>
<td>17.1</td>
<td>11.5</td>
</tr>
<tr>
<td>( s-\eta^2 )</td>
<td>17.0</td>
<td>-</td>
</tr>
<tr>
<td>s-( \eta^1(\text{st}) )</td>
<td>16.4</td>
<td>10.9</td>
</tr>
<tr>
<td>s-( \eta^1(\text{fl}) )</td>
<td>16.5</td>
<td>10.8</td>
</tr>
</tbody>
</table>
The desorption pre-factors are about an order of magnitude larger for the more constrained $p$-$\eta$$^1$ complexes compared with the $s$-$\eta$$^1$ complexes. The desorption pre-factors computed using the $3N$ - 2 model range from $\log(\nu_d) = 14.1$ to 15.5. Thus, treating two of the adsorbate modes as free motions lowers the desorption pre-factors by a factor of about 100, on average. The reaction pre-factors span an overall range from $\log(\nu_r) = 10.8$ to 11.8, and are higher for the $3N - 2$ vs. $3N$ model by about a factor of two. The ratio of desorption to reaction pre-factors $\nu_d/\nu_r$ has values near $5 \times 10^5$ for the $3N$ model, but only $3 \times 10^3$ for the $3N - 2$ model. As shown below, the lower values of $\nu_d/\nu_r$ for the $3N - 2$ vs. $3N$ model produce higher values of the dissociation probability at the temperatures considered and better match experimental findings. The ZPC energies also differ between the $3N - 2$ vs. $3N$ models by values between 0.5 and 1.5 kJ/mol. The differences in kinetic pre-factors have a much more significant effect on the predicted dissociation kinetics.

Kinetic simulations were also conducted to predict the initial dissociation probability as a function of temperature and also product yields obtained during temperature programmed reaction spectroscopy experiments. For the model, the total dissociation probability is given by the following equation,

$$ S_r = \frac{\sum y_i k_{r,i}}{\sum y_i (k_{r,i} + k_{d,i})} $$

(4-12)

where, the equilibrium mole fractions and rate coefficients are temperature dependent. To calculate product yields obtained during TPRS, it is assumed that each desorption and reaction process is first order in the concentration of the appropriate molecular state and numerically integrate the mole balance equations as a function of the sample
temperature, using a constant heating rate of 1 K/s to match prior experimental conditions. At each temperature step in the simulation, the equilibrium condition using the following equation is applied,

\[
[RH]_i(T + \Delta T) = y_i(T + \Delta T) \sum [RH]_i(T)
\]  

(4-13)

where, \([RH]_i(T)\) represents the concentration of molecular state \(i\) determined at temperature \(T\) from numerical integration of the state \(i\) mole-balance equation and \([RH]_i(T + \Delta T)\) represents the concentration of molecular state \(i\) used as input for the numerical integration at the next temperature step. TPRS simulations were conducted from a temperature of 125 to 350 K at which point the concentration of molecularly adsorbed species becomes nearly zero.

Figure 4-6 shows the dissociation probability calculated from the 3\(N\) and 3\(N\) – 2 models along with that obtained in previous experiments. The experimental data is represented by a function derived from a precursor-mediated model for reaction in which propane molecules are assumed to populate only a single molecular state and can either desorb or react from this state. The dissociation probability of propane on PdO(101) were previously measured at temperatures from 250 to 300 K. The 3\(N\) model underestimates the experimentally-determined dissociation probabilities significantly, whereas the predictions of the 3\(N\) – 2 model are only slightly higher than the experimental curve. For example, the measured dissociation probability is 0.20 at 300 K, and the 3\(N\) and 3\(N\) – 2 models predict values of 0.001 and 0.24 at 300 K, respectively. For both models, the difference between the computed results and experimental data grows with increasing temperature. This comparison suggests that the 3\(N\) – 2 model provides more accurate kinetic parameters than the 3\(N\) model.
Figure 4-6. Comparison of initial dissociation probability vs. surface temperature for propane on PdO(101) determined experimentally and computed using the $3N$ and $3N - 2$ models.

To estimate apparent kinetic parameters for the micro-kinetic models, the computed $S(T)$ relations were analyzed using the single-state model that were previously used to analyze experimental data. In this model, the total dissociation probability, in the limit of zero coverage, is given by the equation,

$$S_r = \frac{\alpha k_r}{k_r + k_d}$$  \hspace{1cm} (4-14)

where $\alpha$ is the molecular adsorption probability, assumed to equal unity, and $k_r$ and $k_d$ represent rate coefficients for reaction and desorption from the molecular state, respectively. By comparison with Equation 4-12 derived from the micro-kinetic model, the rate coefficients $k_r$ and $k_d$ may be viewed as effective kinetic parameters. Previously, it has been shown that Equation 4-14 provides an accurate representation
of the measured dissociation probability of propane as a function of the PdO(101) surface temperature when the temperature–dependence of the rate coefficients is assumed to follow Arrhenius equations with constant pre-factors \( \nu \) and activation energies \( E \). Analysis of the experimental data gives an apparent pre-factor and activation energy of \( \nu_d / \nu_r = 2588 \) and \( E_r - E_d = -16.2 \text{ kJ/mol} \) for propane dissociation on PdO(101).\(^{78}\) It is observed that the single-state model accurately fits the \( S(T) \) relations determined from the 3\( N \) and 3\( N - 2 \) models as well. From these fits, we estimate apparent pre-factors and activation energies of \( \nu_d / \nu_r = 1.0 \times 10^6 \) and \( E_r - E_d = -18.1 \text{ kJ/mol} \) for the 3\( N \) model, and \( \nu_d / \nu_r = 5.1 \times 10^3 \) and \( E_r - E_d = -18.4 \text{ kJ/mol} \) for the 3\( N - 2 \) model. The apparent activation energies agree to within about 14\% of the experimental estimate, which is quite good. On the other hand, the apparent pre-factor obtained from the 3\( N \) model is about 200 times larger than the experimental estimate, while the apparent pre-factor obtained from the 3\( N - 2 \) model agrees to within a factor of two of the experimental value.

These comparisons establish that the 3\( N \) model overestimates the apparent pre-factor for desorption \( \nu_d / \nu_r \). Notice that the ratio \( \nu_d / \nu_r \) is proportional to the entropy difference between a gas-phase propane molecule and the transition structure for C-H bond cleavage. Thus, the overly high value of \( \nu_d / \nu_r \) predicted by the 3\( N \) model implies that this model underestimates the entropy of the transition structure for reaction. The 3\( N - 2 \) model treats two of the frustrated modes as free motions and thus predicts a larger entropy of the transition structure. Although this treatment is approximate, the good agreement between the model and experimental \( \nu_d / \nu_r \) value suggests that the 3\( N - 2 \) model accurately reproduces the entropy of the dissociation transition structure.
Importantly, while it can be concluded that the $3N - 2$ model reproduces the apparent pre-factor $\nu_d / \nu_r$, definitive conclusions about the accuracy of the individual $\nu_d$ and $\nu_r$ values cannot be reached because these values are not known from experiment. In prior work, propane desorption spectra has been collected from PdO(101) but the complex nature of the spectra precludes an accurate estimation of the desorption pre-factors.\textsuperscript{78, 109} In the future, it may be possible to obtain more reliable estimates of the desorption pre-factor(s) by performing isothermal measurements of propane desorption rates from PdO(101).

The micro-kinetic models also predict a strong preference for primary C-H bond cleavage in the activation of propane on PdO(101), in agreement with experimental observations. In a previous study, it was estimated that 1-propyl fragments constitute 90\% of the total propyl yield that results from propane dissociation on PdO(101) during TPRS experiments.\textsuperscript{109} To make a comparison with the experimentally-determined bond selectivity, temperature-programmed reaction conditions were simulated for both kinetic models for temperatures increasing from 125 to 350 K. These simulations predict relative yields of 1-propyl groups equal to 99.6\% and 98.8\% for the $3N$ and $3N - 2$ models, respectively, where the corresponding ratios of 1-propyl to 2-propyl fragments are equal to $\sim 257$ and 86. The models thus reproduce the preference for primary C-H bond activation, but they overestimate the selectivity. Several factors could be responsible for the overestimation, including errors in the computed kinetic parameters and deviations from an equilibrium distribution of adsorbed complexes which is assumed in the simulations.
The models predict that dissociation of the p-2\(\eta^1(st)\) and s-\(\eta^1(st)\) complexes make the dominant contributions to the production of 1-propyl and 2-propyl groups on PdO(101), respectively. Higher concentrations of the p-2\(\eta^1(st)\) complexes as well as higher relative dissociation rates of this species are responsible for the preference for primary C-H bond activation that is predicted by the models. For example, the models predict that the relative population of p-2\(\eta^1(st)\) to s-\(\eta^1(st)\) complexes remains greater than unity at temperatures where most of the propane reacts or desorbs, decreasing from a value of 11 to unity as the surface temperature decreases from 150 to 265 K. An even more significant effect is that the kinetic branching strongly favors reaction of the p-2\(\eta^1(st)\) complexes relative to reaction of the s-\(\eta^1(st)\) complexes. The apparent rate coefficients for dissociation of the p-2\(\eta^1(st)\) and s-\(\eta^1(st)\) complexes are defined as \((k_r/k_d)_1\) and \((k_r/k_d)_2\), and an apparent branching ratio for primary C-H bond cleavage as \((k_r/k_d)_1/(k_r/k_d)_2\). This branching ratio is well above unity at all temperatures of the TPRS simulation for both models. For example, the branching ratio computed using the 3\(N-2\) model decreases from about 500 to 8.5 as the surface temperature increases from 150 to 350 K. The apparent activation energy for dissociation is 9.5 kJ/mol lower for the p-2\(\eta^1(st)\) vs. s-\(\eta^1(st)\) complex, and is responsible for the high branching ratio for primary C-H bond activation. In fact, entropic factors favor dissociation of the s-\(\eta^1(st)\) complex over the p-2\(\eta^1(st)\) complex. For the 3\(N-2\) model, the apparent reaction pre-factor is 24 times higher for the s-\(\eta^1(st)\) vs. the p-2\(\eta^1(st)\) complex. Overall, the kinetic models predict a high selectivity for primary C-H bond cleavage of propane on PdO(101), in agreement with experimental findings, and provide insights for understanding kinetic factors that determine this initial bond selectivity.
4.4 Summary

DFT-D3 calculations have been used to investigate pathways for initial C-H bond cleavage of propane complexes adsorbed on the PdO(101) surface. The calculations predict that each adsorbed propane $\eta^1$ complex can undergo facile C-H bond cleavage on PdO(101), where the energy barrier for dissociation is less than the barrier for desorption. It is also found that the propane $\eta^2$ complexes are unable to directly undergo C-H bond cleavage on PdO(101) due to steric interactions with adjacent surface atoms, but can readily transform to $\eta^1$ configurations.

The calculations predict that activation of the propane p-2$\eta^1$(st) complex is the preferred pathway for C-H bond cleavage of propane on PdO(101), and gives rise to a strong preference for primary C-H bond activation. The calculations suggest that two factors are responsible for the preference toward primary C-H bond activation of propane on PdO(101). The first is that propane molecules tend to populate the p-2$\eta^1$ states and thus preferentially bind in configurations in which only primary C-H bonds interact strongly with the surface. Also, charge analysis of the transition structures shows that propane C-H bond cleavage is heterolytic on PdO(101), and suggests that greater substituent polarization produces a more stabilizing charge distribution within the 1-propyl vs. 2-propyl TSs, which in turn causes the intrinsic energy barrier for primary C-H bond activation to be lower than that for secondary C-H bond activation of the p-2$\eta^1$ vs. s-$\eta^1$ complexes, respectively.

The kinetics of propane dissociation on PdO(101) have also been simulated using micro-kinetic models derived from the DFT-D3 structures, and it is found that the simulations reproduce the apparent activation energy for propane dissociation on
PdO(101) to within 14% of the measured value. The simulations demonstrate that the computed pre-factors are highly sensitive to the approach taken for calculating partition functions of the adsorbed alkane structures. It is observed that modeling all of the adsorbate motions as harmonic vibrations underestimates the entropy of the transition structure for C-H bond cleavage, causing the apparent pre-factor for reaction to be more than two orders of magnitude higher than the experimental estimate. In contrast, the kinetic model accurately reproduces the apparent pre-factor for reaction when two of the frustrated adsorbate motions are treated as free motions. While approximate, the results of the $3N-2$ model highlight the need to accurately determine the entropic contributions made by weakly-hindered motions in the dissociation of alkanes on solid surfaces.
CHAPTER 5
PATHWAYS AND KINETICS FOR THE C-H BOND CLEAVAGE OF METHANE AND ETHANE ON PdO(101)

5.1 Motivation

Activating hydrocarbons on transition metal oxide surfaces has gained significant interest since it serves as a key step in the catalytic combustion of natural gas, exhaust gas remediation in automobiles, fuel cell catalysis and selective oxidation processes. Among the saturated hydrocarbons, methane activation is of particular interest because natural gas consists predominantly of methane (70-90%). Developing more efficient and selective methods for activating methane would create new opportunities to produce higher hydrocarbons and even organic oxygenates of greater economic value. However, methane activation poses a significant challenge because the symmetric and non-polar tetrahedral structure of the molecule strengthens C-H bonds and weakens interactions with many catalytic surfaces. Palladium oxide (PdO) appears to be exceptional as this material displays high activity in promoting the complete oxidation of alkanes. In fact, the high activity of oxide-supported Pd catalysts in oxygen rich applications of catalytic combustion has been attributed to the formation of PdO, though the exact nature of the reaction mechanism on oxidized Pd surfaces is not completely understood and remains a focus of study. Recent in situ investigations have shown that the PdO(101) facet develops preferentially during the oxidation of Pd(100) and that PdO(101) formation coincides with increased rates of methane oxidation during reaction at millibar pressures. These findings suggest that alkane chemistry on the PdO(101) surface plays a central role in commercial applications of Pd-catalyzed alkane oxidation. Model investigations of PdO(101) surface chemistry may thus offer key insights for understanding applications of oxidation catalysis.
In prior work, it has been determined that the dissociation of propane and higher alkanes is highly facile on the PdO(101) surface, with initial C-H bond cleavage occurring below 225 K in ultrahigh vacuum (UHV).\textsuperscript{78, 109} It is also found that alkane activation on PdO(101) occurs \textit{via} a precursor-mediated mechanism wherein a molecularly adsorbed state acts as the precursor for initial dissociation and a kinetic competition between dissociation and desorption of the precursor determines the net probability for dissociation. Both computational and experimental studies provide evidence that alkanes form strongly-bound $\sigma$-complexes on PdO(101) by datively bonding with coordinatively unsaturated (cus) Pd atoms, and that the alkane $\sigma$-complexes serve as precursors for initial C-H bond cleavage.\textsuperscript{79} DFT further shows that coordination with the Pd center significantly weakens alkane C-H bonds, thus lowering the energy barriers for C-H bond cleavage.

As is well known, conventional DFT calculations do not account for dispersion interactions, and consequently underestimate alkane binding energies on solid surfaces. For this reason, the alkane C-H bond cleavage barriers that are predicted by conventional DFT compare poorly with the so-called apparent energy barriers for dissociation, which are measured relative to the gas-phase energy level. An apparent energy barrier for dissociation is also equal to the difference between the barrier for alkane dissociation and the barrier for desorption, each measured relative to the initial molecularly adsorbed state. As an example, conventional DFT predicts a binding energy of only \(~16\) kJ/mol for the methane $\sigma$-complex on PdO(101) and a C-H bond cleavage barrier of \(~55\) kJ/mol from the adsorbed state, which gives an apparent dissociation barrier of \(39\) kJ/mol.\textsuperscript{96} However, both TPD experiments and dispersion-corrected DFT-
D3 calculations reveal that the binding energy of methane on PdO(101) is ~40 kJ/mol.\(^{40}\) This comparison implies that the true value of the apparent dissociation barrier for methane on PdO(101) is considerably lower than the value predicted by conventional DFT.

It has been demonstrated in chapter 3 and chapter 4 that the dispersion-corrected DFT-D3 method accurately reproduces the binding energies of \(n\)-alkane \(\sigma\)-complexes on PdO(101),\(^{40}\) and also reproduces the apparent activation energy for propane dissociation on PdO(101) to within 15\% of the experimentally determined value.\(^{124}\) The high accuracy with which the DFT-D3 method appears to predict apparent barriers for alkane C-H bond cleavage on PdO(101) is promising and is indeed essential for developing reliable kinetic models of alkane dissociation on solid surfaces.

Modeling precursor-mediated surface reaction kinetics also requires an accurate representation of the entropic contributions for dissociation and desorption. Toward this end, models for computing kinetic pre-factors which govern propane dissociation on PdO(101), where the model parameters are determined from relaxed structures obtained using DFT-D3 has been examined in chapter 4.\(^{124}\) Those results show that a so-called \(3N-2\) model, in which two of the frustrated adsorbate motions are treated as free motions, reproduces the apparent pre-factor for propane dissociation on PdO(101) to within about a factor of two. Because DFT-D3 also accurately reproduces the apparent energy barrier for dissociation, the \(3N-2\) model predicts dissociation probabilities of propane on PdO(101) that agree well with experimental measurements.

In this chapter, DFT-D3 is used to investigate pathways for C-H bond activation of methane and ethane \(\sigma\)-complexes on PdO(101) as well as initial reactions of
adsorbed CH$_3$ groups. Micro-kinetic models of the precursor-mediated dissociation of methane and ethane on PdO(101) are also evaluated, and it is found that the $3N - 2$ model predicts kinetic pre-factors and dissociation probabilities that agree well with values obtained from the literature. Of particular significance is finding out that the $3N - 2$ model predicts desorption pre-factors for small alkanes from PdO(101) that agree closely with estimates made using a correlation that was recently reported by Campbell and Sellers.\textsuperscript{125}

5.2 Computational Details

The calculations reported in this paper employ conventional (DFT) and dispersion-corrected (DFT-D3) density functional theory. The DFT-D3 method is an extension of conventional DFT calculations implemented through the Vienna \textit{ab initio} simulation package\textsuperscript{84-86} and incorporates the dispersion technique (D3) developed by Grimme \textit{et al.}\textsuperscript{48,113} The DFT-D3 method computes dispersion effects separately and adds the dispersion energies and forces ($E_{\text{disp}}, F_{\text{disp}}$) to the energies and forces determined through conventional DFT electronic relaxations ($E_{\text{dft}}, F_{\text{dft}}$). The total ionic forces ($F_{\text{dft}} + F_{\text{disp}} = F_{\text{dft-d3}}$) are then relaxed using a limited memory Broyden-Fletcher-Goldfarb-Shanno optimization method\textsuperscript{59} until the forces on all unconstrained atoms are less than 0.01 eV/Å. The parameters used for the DFT calculation are the same as those used in earlier studies of the PdO(101) surface.\textsuperscript{40,79,96,114} Projector augmented wave (PAW) pseudo potentials\textsuperscript{89} provided in the VASP database are used along with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional\textsuperscript{33} and a plane wave cutoff of 400 eV. Energy calculations to determine $E_{\text{dft}}$ are done using the residual minimization method with direct inversion in the iterative subspace for
electronic relaxations accelerated using Methfessel-Paxton Fermi-level smearing\textsuperscript{101} with a Gaussian width of 0.1 eV. The dispersion energy ($E_{\text{disp}}$) used in the DFT-D3 formulation is given by Equation 5-1, where the pairwise interactions are summed over all the atoms within a cutoff radii of 50 \text{"Å"}. $E_{\text{disp}}$ is a function of $n$th order inter-nuclear distances ($r_{AB}^{-n}$), dispersion coefficients ($C_{AB}^{n}$) that have been computed \textit{ab initio} by time-dependent DFT, a scaling fraction ($s_{n}$) that ensures asymptotic exactness and a damping function ($f_{d,n}(r)$). The parameters have been directly taken from the most recent implementation of dispersion in DFT calculations by Grimme \textit{et al.}\textsuperscript{48} The study presented in chapter 3 shows that binding energies of $n$-alkane adsorption on PdO(101) predicted by DFT-D3 are within 2.5 kJ/mol (< 5%) of the experimental-derived values for alkane chain lengths up to $n$-butane.\textsuperscript{40}

$$E_{\text{disp}} = - \frac{1}{2} \sum_{AB} \left[ s_6 \frac{C_{6}^{AB}}{r_{AB}^{6}} f_{d,6}(r_{AB}) + s_8 \frac{C_{8}^{AB}}{r_{AB}^{8}} f_{d,8}(r_{AB}) \right]$$ (5-1)

The PdO(101) thin film used in the experimental studies is grown on a Pd(111) substrate at 500 K by oxidizing the metal surface in UHV using an oxygen atom beam. The generated film is \textasciitilde13 \text{"Å"} thick and consists of \textasciitilde3 ML of oxygen atoms, where 1 ML is defined as the Pd(111) surface atom density of $1.53 \times 10^{15}$ cm$^{-2}$. The stoichiometric PdO(101) surface comprises of alternating rows of coordinatively unsaturated (\textit{cus})/threefold and coordinatively saturated/fourfold (4\textit{f}) Pd and O atoms as shown in Figure 5-1. The coordinative environment associated with each \textit{cus}-Pd atom resembles a square planar Pd complex with a coordination vacancy directed away from the surface and three oxygen ligands. The presence of a coordination vacancy renders high activity to the \textit{cus} metal sites as observed in earlier studies.\textsuperscript{83, 88, 94, 114, 115} PdO(101) surface has
a total atomic coverage of 1.4 ML (1.4 times that on Pd(111)) which is equally distributed between cus and 4f Pd and O atomic species.

Computational model for the PdO(101) surface is derived by slicing bulk crystalline PdO along the (101) plane, followed by straining the model to match the lattice parameters reported by low energy electron diffraction experiments ($a = 3.057 \, \text{Å}, b = 6.352 \, \text{Å}$). The strained model is relaxed after fixing the bottom layer for stability. The bulk terminated PdO(101) surface is defined by a rectangular unit cell with lattice vectors $\vec{a}$ and $\vec{b}$ (shown in Figure 5-1) that corresponds to [010] and [101] crystallographic directions of the PdO crystal, respectively.

Figure 5-1. Stoichiometric PdO(101) surface. Comprises of 0.35 ML of cus-Pd, cus-O, 4f-Pd and 4f-O each. $\vec{a}$ and $\vec{b}$ represent the [010] and [101] crystallographic directions of bulk PdO. The cus-Pd atoms aligned along the $\vec{a}$ direction collectively form the cus-Pd row.
The computational model of the PdO(101) surface used in the study consists of four layers totaling a thickness of ~9 Å and omits the Pd(111) metal substrate. Previous studies show that the thickness of 9 Å is sufficient enough to ignore the metal substrate as increasing the layer thickness does not affect the interaction between the chemisorbing species and the surface. A vacuum spacing of ~20 Å is maintained normal to the surface in order to eliminate spurious periodic interactions in this direction. A 2 × 4 × 1 (4 × 2 × 1) Monkhorst-Pack k-point mesh has been used for the 2 × 2 (4 × 1) unit cell sizes, respectively. The 2 × 2 (4 × 1) unit cell sizes are derived by doubling the unit cell size along \( \vec{a} \) and \( \vec{b} \) (quadrupling the unit cell size along \( \vec{a} \) alone). The larger cell sizes ensure that there is sufficient distance between chemisorbing species and thus minimal coverage effects.

The adsorption/binding energies reported in this study \( (E) \) are defined as the difference between the sum of total energies (electronic plus dispersion, \( E_{dft-d3} \)) for the isolated molecule \( (E_{iso}) \) and bare surface \( (E_{bare}) \) with that of the chemisorbed molecule/surface system \( (E_{chemisorb}) \) as represented in Equation 5-2.

\[
E = [E_{bare} + E_{iso}] - E_{chemisorb}
\]  

5-2

The binding energies for methane and ethane on PdO(101) are reported based on a single molecule (kJ/mol CH₄ or C₂H₆) chemisorbed on a 2 × 2 or 4 × 1 PdO(101) supercell for which the coverage is equal to 0.0875 ML. The simulated coverage is close to experimental estimates of the saturation coverage (~0.09 ML). The ethane and methane \( \sigma \)-complexes in the supercells are separated by ~6.35 Å at 0.0875 ML coverage and hence interact only weakly with one another. The various configurations
determined on the surface are confirmed to be true minima by performing normal mode analyses, where the frequencies of the vibrational modes are calculated by fixing the surface atoms while leaving the chemisorbed molecule unconstrained. The computed vibrational frequencies are used to calculate zero-point corrections for the total energies. Activation pathways for methane and ethane are determined using climbing nudged elastic band (NEB) method, and normal mode analyses are performed on the transition states to confirm the presence of a single imaginary frequency. Vibrational frequencies computed for the different states are employed to determine desorption and reaction rate constants used in the micro-kinetic model described in a subsequent section.

5.2 Results and Discussion

5.2.1 Molecular Chemisorption of Methane and Ethane on PdO(101)

Previous chapters illustrate that alkanes form \( \sigma \)-complexes on PdO(101) by datively bonding with \( \text{cus} \)-Pd atoms of the surface, and the most stable \( \sigma \)-complexes of methane through \( n \)-pentane on PdO(101) determined using DFT-D3 are also reported.\(^79\) Here, additional stable configurations of ethane \( \sigma \)-complexes on PdO(101) that have been identified computationally are presented. As reported previously, DFT-D3 calculations find only one methane \( \sigma \)-complex on PdO(101) that is consistent with the strongly-bound state observed in TPD experiments.\(^40\) The favored methane \( \sigma \)-complex on PdO(101) corresponds to an \( \eta^2 \) complex in which a H-C-H bond angle straddles a \( \text{cus} \)-Pd atom and the two downward-oriented H-atoms align parallel to the row of \( \text{cus} \)-Pd atoms (Figure 5-2 A)). The \( \eta^2 \) geometry produces a three-center dative interaction between two H-atoms of the alkane molecule and the \( \text{cus} \)-Pd atom. According to DFT-
D3, the CH₄ \eta^2 complex on PdO(101) has a zero-point corrected binding energy of 40.5 kJ/mol, which agrees well with the prior experimental estimate.⁴⁰

Using DFT-D3, three stable C₂H₆ complexes on PdO(101) are identified and it is found that the binding energies of these complexes are within 3.5 kJ/mol of one another. In the most stable C₂H₆ complex, one of the CH₃ groups adopts an \eta^2 bonding configuration on top of a cus-Pd atom, while the other CH₃ group is directed away from the surface and toward the neighboring cus-O atom (Figure 5-2 B)). This complex is designated as the \eta^2(+) complex, where the “+” symbol indicates that the remote CH₃ group is directed toward the cus-O atom. In the ethane \eta^2(-) complex, the Pd-coordinated CH₃ group adopts the same bonding configuration with the cus-Pd atom as in the \eta^2(+) complex but the remote CH₃ group is oriented toward the adjacent 4f-O atom(Figure 5-2 C)). The \eta^2(+) and \eta^2(-) configurations are related by a 180° rotation of the ethane molecule about the dative bond with the cus-Pd atom. DFT-D3 predicts that the ethane \eta^2(+) and \eta^2(-) complexes on PdO(101) are nearly degenerate in energy, with binding energies of 56.4 and 55.2 kJ/mol, respectively.

A third ethane configuration on PdO(101) that may be classified as an \eta¹ complex is also identified. In the ethane \eta¹ configuration, the C-C bond lies along the cus-Pd row and a H-atom of one of the CH₃ groups experiences an \eta¹ dative interaction with a cus-Pd atom. A hydrogen atom on the second CH₃ group also interacts with a cus-Pd atom, but this interaction is weaker than the H-Pd dative bond at the neighboring site. In the top view of the ethane \eta¹ complex shown in Figure 5-2 D), the H-Pd dative bond occurs at the CH₃ group that is closer to the bottom of the image, while the “upper” CH₃ group (in the top view) is not close enough to a cus-Pd atom to form an optimal
dative bond. It is noted that, unlike ethane, the methyl groups of propane are separated
by a sufficient distance to allow single H-Pd dative bonds to form at each CH₃ group.
The binding energy of the \( \eta^1 \) ethane complex is 53.0 kJ/mol according to DFT-
D3. The similar binding energies of the ethane \( \sigma \)-complexes on PdO(101) suggests that each of
these complexes can attain appreciable populations on PdO(101) at typical
temperatures of interest.

![Figure 5-2. Top and front views of methane and ethane \( \sigma \)-complexes on PdO(101) surface. A) Methane \( \eta^2 \). B) Ethane \( \eta^2(+) \). C) Ethane \( \eta^2(-) \). D) Ethane \( \eta^1 \).](image)

Both DFT and DFT-D3 predict that the formation of alkane \( \sigma \)-complexes on
PdO(101) results in significant softening (red-shifted from gas-phase values) of
molecular vibrational modes. For the methane \( \eta^2 \) complex, motions of the Pd-
coordinated C-H bonds involving asymmetric stretching along \( \bar{a} \), symmetric stretching
along \( \bar{a} \) and symmetric stretching along \( \bar{b} \) undergo red-shifts of 206, 166 and 106 cm⁻¹
from gas-phase values according to DFT, and by 241, 202 and 116 cm⁻¹ according to
DFT-D3. The slightly larger red-shift estimated using DFT-D3 is due to the closer
proximity of the methane molecule to the cus-Pd atom. Similarly, for the ethane complexes, the DFT-D3 calculations predict a softening in the range of 175-205 and 270-320 cm$^{-1}$ for symmetric and asymmetric C-H stretching modes, respectively. Significant C-H bond softening is a strong indication that dative interactions with cus-Pd atoms weaken the alkane C-H bonds.

5.2.2 Pathways for Methane Activation on PdO(101)

The C-H bond activation pathway of CH$_4$ on PdO(101) is investigated using both DFT and DFT-D3 to quantify the effects of dispersion interactions on the computed energy barrier as well as to obtain a more accurate estimate of the apparent energy barrier for dissociation measured relative to the gas-phase energy level. In chapter 2, pathways for CH$_4$ activation on PdO(101) via cleavage of an activated vs. a non-activated C-H bond were reported. Note that the two Pd-coordinated C-H bonds of the $\eta^2$ complex are designated as “activated” while the other two C-H bonds are “non-activated” (Figure 5-2 A)). Excluding zero-point corrections, conventional DFT predicts energy barriers of 167 vs. 64 kJ/mol for cleavage of a non-activated vs. activated C-H bond of CH$_4$ on PdO(101), respectively. These results demonstrate that coordination with the Pd center lowers the activation barrier for methane C-H bond scission by more than 100 kJ/mol and thus that the Pd-coordinated C-H bonds of alkanes on PdO(101) are far more amenable to cleavage than the non-activated bonds.

Figure 5-3 shows energy diagrams computed using DFT and DFT-D3 for the preferred CH$_4$ activation pathway on PdO(101) in which one of the Pd-coordinated C-H bonds is cleaved. In the energy diagram the zero of energy is taken as the isolated molecule plus the adsorbate-free PdO(101) surface. Figure 5-3 also shows structural
representations of the initial state (IS), transition state (TS) and final states (FS). In the reaction pathway, the methane molecule rotates about the \textit{cus}-Pd atom and transfers a H-atom from one of the Pd-coordinated C-H bonds to the neighboring \textit{cus}-O atom, resulting in a HO\textit{cus} species and a CH$_3$-Pd$_{\text{cus}}$ species. Other investigators have confirmed the minimum energy pathway for methane activation on PdO(101).$^{107, 108}$ Analysis of the atomic charges using the DDEC method$^{57}$ shows that methane C-H bond cleavage occurs heterolytically on PdO(101), in agreement with recent findings for propane activation on the oxide surface.$^{124}$

![Diagram](image.png)

Figure 5-3. Initial, transition and final states for the initial C-H bond activation of methane $\eta^2$ complex on PdO(101). Diagram illustrates zero-point corrected energies predicted by conventional and dispersion-corrected DFT.

The pathways predicted by DFT and DFT-D3 are nearly identical. The main difference is that the molecular species are slightly closer to the surface Pd atoms in the DFT-D3 derived pathway due to the additional molecule-surface attraction that results
from the dispersion forces. It is determined that including dispersion interactions in the DFT-D3 calculations cause the energy level of each stationary state to down shift by nearly the same amount (~25 kJ/mol) within a few kJ/mol. As a result, DFT and DFT-D3 predict similar energy barriers relative to the initial molecularly adsorbed state (IS), with zero-point corrected values of 55.3 and 55.2 kJ/mol, respectively, as well as similar values of the reaction exothermicity defined as the energy difference between the FS and IS (-34.0 vs. -36.0 kJ/mol). Table 5-1 gives the zero-point corrected energies of the IS, TS and FS predicted by DFT-D3. Hereafter, the difference between the TS and the IS is referred to as the intrinsic reaction barrier for alkane C-H bond cleavage.

Table 5-1. Zero-point corrected binding energies (3N vibrational modes) of different states evolving from the activation of methane $\sigma^2$ and ethane $\sigma^2(+), \sigma^2(-)$ and $\eta^1$ complexes on PdO(101) surface. Note that $(\Delta E_{r,i}^z - \Delta E_{d,i}^z)$ represents apparent reaction barrier.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Initial state $(\Delta E_{d,i}^z)$</th>
<th>Transition state $(\Delta E_{d,i}^z - \Delta E_{r,i}^z)$</th>
<th>Final state $(E_{FS})$</th>
<th>Reaction barrier $(\Delta E_{r,i}^z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane $\sigma^2$</td>
<td>39.1</td>
<td>-16.1</td>
<td>75.1</td>
<td>55.2</td>
</tr>
<tr>
<td>Ethane $\sigma^2(+)</td>
<td>55.3</td>
<td>-12.6</td>
<td>94.7</td>
<td>67.9</td>
</tr>
<tr>
<td>Ethane $\sigma^2(-)$</td>
<td>56.4</td>
<td>-0.1</td>
<td>95.8</td>
<td>56.4</td>
</tr>
<tr>
<td>Ethane $\eta^1$</td>
<td>53.5</td>
<td>1.5</td>
<td>95.5</td>
<td>52.0</td>
</tr>
</tbody>
</table>

* Energies are reported in kJ/mol C$_N$H$_{2N+2}$

The apparent reaction barrier is defined with respect to the gas-phase reference energy and is equal to the difference between the energy barriers for the methane $\sigma$-complex to react $(\Delta E_{r}^z)$ vs. desorb $(\Delta E_{d}^z)$). The apparent reaction barrier is an important factor in determining the kinetic branching probability for adsorbed CH$_4$ to dissociate on the PdO(101) surface. Because dispersion interactions stabilize the adsorbed structures relative to the gas-phase reference state, the apparent reaction barrier computed using DFT-D3 is lower than that obtained using conventional DFT. The apparent barrier
determined using DFT-D3 may also compare well with experimental data because both
dispersion and electronic interactions are taken into account. Indeed, it has been
reported that DFT-D3 provides a value of the apparent reaction barrier for propane
activation on PdO(101) that agrees to within 15% of experimental estimates.\textsuperscript{124} For CH\textsubscript{4}
activation on PdO(101), apparent reaction barriers of 16.1 and 40.3 kJ/mol are
predicted using DFT-D3 and DFT, respectively, where the barriers are corrected for
zero-point vibrational energy. Since the apparent reaction barrier is positive (i.e., lies
above the gas-phase level), methane dissociation is expected to occur on PdO(101) to
a negligible extent during low temperature TPD experiments, which is consistent with
previous findings.\textsuperscript{79} Notably, however, the apparent reaction barrier predicted for
methane dissociation on PdO(101) is lower than the apparent activation energies that
have been reported for methane dissociation on crystalline transition metal surfaces.\textsuperscript{61}
Among the metal surfaces that have been studied, Ir(110) exhibits the highest reactivity
toward methane and the apparent activation energy for dissociation is reported to be 21
kJ/mol.\textsuperscript{126, 127} The DFT-D3 calculations thus suggest that the PdO(101) surface has a
higher activity toward methane dissociation than many metallic surfaces. This
conclusion is consistent with reports that PdO formation is responsible for the high
activity of supported Pd catalysts in the catalytic combustion of methane.\textsuperscript{4, 9, 65-70} The
high reactivity of PdO(101) toward methane C-H bond cleavage arises in part from the
dative interaction between CH\textsubscript{4} and \textit{cus}-Pd atom.

\textbf{5.2.3 Reactions of Adsorbed CH\textsubscript{3} on PdO(101)}

DFT-D3 is used to identify plausible reaction steps that occur after the initial C-H
bond activation of CH\textsubscript{4} on PdO(101). Figure 5-4 shows reaction steps identified for the
CH\textsubscript{3}-Pd\textsubscript{cus} species. The calculations show that diffusion of the CH\textsubscript{3} group along the \textit{cus-
Pd row is relatively facile, with an energy barrier of only 59.6 kJ/mol relative to the initial state. Further reaction rather than recombination back to CH₄ should be favored because the diffusion barrier lies below the gas-phase energy level and is smaller than the recombination barrier. The results also show that the binding energy of the CH₃-Pd cus species is 14.5 kJ/mol higher when adsorbed next to a HO cus vs. next to an empty cus-O group, which means that the barrier is lower for the CH₃ group to hop back to its original binding site than to move away from the HO cus group.

A pathway is identified for the CH₃ group to dehydrogenate to produce a CH₂ group plus a HO cus group. This reaction is a concerted process in which the CH₃ group transfers a H-atom to an neighboring cus-O atom while simultaneously moving into the cus-Pd bridge site that is located between adjacent HO cus groups. The energy barrier for CH₃ dehydrogenation is 138.7 kJ/mol if the reaction initiates when the CH₃ group is next to an empty cus-O atom; the barrier is 155.2 kJ/mol if the CH₃ group dehydrogenates from its original binding site. The CH₃ dehydrogenation reaction on PdO(101) is endothermic by 16.9 kJ/mol so the reverse reaction that restores the CH₃-Pd cus species will be favored unless other reactions compete effectively for the CH₂ and HO cus species. Also, the CH₃ dehydrogenation barrier is significantly larger than the barrier for C-H bond cleavage of the CH₄ μ² complex (138.7 vs. 55.2 kJ/mol), which suggests that the rate of CH₃ dehydrogenation is lower than the initial CH₄ activation rate and may thus represent a rate determining step for the complete oxidation of methane on PdO(101).
Figure 5-4. Energy diagram illustrating reactions of the CH₃-Pd₈ species on PdO(101) after initial CH₄ activation. The panel on the left shows reactions leading to CH₃ dehydrogenation, and the panel on the right shows the pathway for CH₃O₂ formation. Energies have been zero-point corrected.
The reaction energetics further suggest that CH$_3$-Pd$_{cus}$ species can accumulate at temperatures where CH$_4$ activation readily occurs because the steps for both CH$_3$ dehydrogenation and recombination back to CH$_4$ are more strongly activated than dissociation of the CH$_4$ complex. Such behavior is consistent with experimental observations of the oxidation of propane and $n$-butane on PdO(101).$^{78,96}$ In particular, prior TPRS experiments provide evidence that propane and $n$-butane $\sigma$-complexes dissociate on PdO(101) below about 225 K via cleavage of a single C-H bond, and that the resulting alkyl fragments remain stable on the surface up to about 400 K at which point they are completely oxidized to CO$_2$ and H$_2$O by reactions with the PdO(101) surface. An implication is that a reaction step(s) involving the alkyl groups controls the overall rate of alkane oxidation on PdO(101) during TPRS. The present results reveal that dehydrogenation of a CH$_3$ group is more energetically demanding than initial CH$_4$ activation and might act as the rate limiting step for complete oxidation. A study using high-resolution core level spectroscopy and DFT to examine the reduction of the PdO(101) surface by H$_2$ reported pathways for HO$_{cus}$ groups to form water with rate-limiting barriers near 90 kJ/mol.$^{128}$ This barrier to H$_2$O formation agrees well with the observation of a water TPRS peak at 340 K associated with the initial C-H bond cleavage for propane and $n$-butane on PdO(101).$^{78,96}$ These studies reveal that oxygen vacancies will be present with the alkyl groups and may play a role in activating the second C-H bond during TPRS experiments. Investigations of additional reaction steps, including the potential role of oxygen vacancies, leading to the complete oxidation of methane on PdO(101) are needed to test this idea.
The hopping of a methyl group from a \textit{cus}-Pd to a \textit{cus}-O atom to generate a CH$_3$O$_{\text{cus}}$ group on the PdO(101) surface (see Figure 5-4) is also investigated. The DFT-D3 calculations predict an energy barrier of 138.4 kJ/mol for CH$_3$ hopping to a \textit{cus}-O atom, and show that the reaction is endothermic by 40.1 kJ/mol, which indicates that the CH$_3$-O$_{\text{cus}}$ bond is weaker than the CH$_3$-Pd$_{\text{cus}}$ bond on the PdO(101) surface. For comparison, Blanco-Rey \textit{et al.} report that CH$_3$ groups preferentially bind on the \textit{cus}-O sites rather than the 4$f$ Pd sites of the stoichiometric PdO(100) surface.$^{129}$ Methoxy formation may compete with CH$_3$ dehydrogenation on PdO(101) since the energy barriers are comparable for these reactions. However, methoxy formation is also less energetically favorable than CH$_3$ dehydrogenation so the reverse reaction (CH$_3$O$_{\text{cus}}$ to CH$_3$-Pd$_{\text{cus}}$) should occur more quickly than the reverse of the dehydrogenation step, unless the methoxy groups undergo additional chemical transformations once formed.

5.2.4 Pathways for Ethane Activation on PdO(101)

A viable C-H bond cleavage pathway for each of the adsorbed ethane complexes on PdO(101) is identified. As observed with methane, dispersion interactions cause a nearly constant downshift in the energy levels of each stationary state along a given ethane reaction pathway. The energy levels computed using DFT-D3 vs. DFT are lower by ~34, 35 and 39 kJ/mol for the states associated with activation of the ethane \(\eta^2(+)\), \(\eta^2(-)\) and \(\eta^1\) complexes, respectively. The \(\eta^1\) complex experiences slightly greater stabilization from dispersion interactions than the \(\eta^2\) complexes because the non-activated CH$_3$ group of the \(\eta^1\) complex is closer to the surface. The relative energy differences among the adsorbed states differ only slightly between the DFT and DFT-D3 calculations. For example, conventional DFT predicts intrinsic reaction barriers of 67.0,
58.2 and 52.8 kJ/mol, while DFT-D3 predicts barriers of 67.9, 56.4 and 52.0 kJ/mol for the ethane $\eta^2(+)$, $\eta^2(-)$ and $\eta^1$ complexes, respectively. Notice that the intrinsic reaction barriers for the ethane $\eta^2(-)$ and $\eta^1$ complexes are similar to that found for the methane $\eta^2$ complex, whereas the intrinsic barrier for activating the ethane $\eta^2(+) $ complex is higher by more than 11 kJ/mol. Steric repulsion appears to increase the dissociation barrier of the ethane $\eta^2(+) $ complex relative to the other adsorbed states, as discussed below.

Figure 5-5 shows the energy diagram and structural representation of the IS, TS and FS for the reaction pathways determined using DFT-D3 for activation of the ethane $\eta^2(+) $, $\eta^2(-)$ and $\eta^1$ complexes on PdO(101). Table 5-1 gives the corresponding zero-point corrected energies relative to the gas-phase reference. Each of the ethane complexes on PdO(101) follows a similar pathway for C-H bond activation in that a Pd-coordinated C-H bond transfers a H-atom to a neighboring cus-O atom to produce a HO cus species and an C2H5-Pd cus species. Interestingly, the intrinsic reaction barriers differ considerably for the ethane $\eta^2(+) $ and $\eta^2(-)$ complexes, with values of 67.9 and 56.4 kJ/mol, respectively, even though these complexes adopt similar $\eta^2$ bonding configurations with a cus-Pd atom.
Figure 5-5. Energy diagram illustrating initial, transition and final states for the initial C-H bond activation of ethane $\eta^2(\text{+})$, $\eta^2(\text{-})$ and $\eta^1$ complexes on PdO(101). Energies have been zero-point corrected.
Examination of the structural changes along the reaction pathways clarifies why the reaction barriers differ for the ethane $\eta^2(\pm)$ complexes. In the reaction pathway for the $\eta^2(\pm)$ complex, the ethane molecule rotates approximately about its C-C bond to bring one of the Pd-coordinated C-H bonds into position for H-transfer to the cus-O atom. During the motion from the IS to the TS, the non-activated CH$_3$ group of the $\eta^2(\pm)$ complex moves closer to the cus-O atom by 0.3 Å and appears to experience a repulsion by the H-atom that is transferred. Activation of the $\eta^2(\mp)$ complex also involves a molecular rotation to bring a Pd-coordinated C-H bond into position for H-transfer to a cus-O atom. However, in this case, the ethane molecule rotates approximately about a line that passes through the Pd-coordinated CH$_3$ group and is parallel with the surface normal. This rotation maintains a relatively large separation between the non-activated CH$_3$ group and the surface oxygen atoms and causes the C-C bond to become nearly parallel with the cus-Pd row as the molecule reaches the TS. The dissociation pathways thus suggest that repulsion between the non-activated CH$_3$ group and the HO$_{cus}$ moiety increases the intrinsic dissociation barrier of the ethane $\eta^2(\pm)$ complex on PdO(101) by about 11.5 kJ/mol. In contrast, steric repulsions appear to have little effect on activation of the $\eta^2(\mp)$ complex given that this species has a similar intrinsic reaction barrier as the methane $\eta^2$ complex (56.4 vs. 55.3 kJ/mol).

Results for the ethane $\eta^2(\pm)$ complex are analogous to previous finding (Chapter 4) that steric repulsions prevent a propane $\eta^2$ complex from dissociating on PdO(101). In that case, a dissociation pathway for a so-called propane s-$\eta^2$ complex that coordinates with a cus-Pd atom through its CH$_2$ group (i.e., a “secondary” C-H bond) could not be identified. Rather than reacting, the propane s-$\eta^2$ complex rotates
into an $\eta^1$ configuration along the *cus*-Pd row from which facile dissociation can occur. Similarly, the ethane $\eta^2(+)$ complex only needs to overcome a small barrier ($< 5$ kJ/mol) to rotate into the $\eta^1$ configuration. A reaction pathway that directly connects the $\eta^2(+) IS$ to the $\eta^2(-)$ TS cannot be determined and thus may be concluded that steric repulsion also prevents the ethane $\eta^2(+) complex from directly accessing the lower energy TS that is sampled by the $\eta^2(-)$ complex during dissociation. Overall, these results demonstrate that steric effects can have an important influence on the C-H bond activation pathways of alkanes on PdO(101).

Among the ethane complexes that we identified, the ethane $\eta^1$ complex must overcome the smallest energy barrier (52.0 kJ/mol) to dissociate on PdO(101). In the dissociation pathway, the ethane $\eta^1$ complex rotates approximately about the surface normal to bring a Pd-coordinated C-H bond into position for H-transfer to a *cus*-O atom (Figure 5-5). After the TS, the ethyl group rotates into a final configuration that is very similar to the ethyl-Pd$\text{cus}$ species that is produced by dissociation of the $\eta^2(-)$ complex. As mentioned above, the binding energies of the ethane complexes on PdO(101) lie within a 3.4 kJ/mol range, with the $\eta^2(-)$ complex having the highest binding energy and the $\eta^1$ complex the lowest. As such, each adsorbed state is likely to be significantly populated at reaction temperatures. In contrast, the apparent dissociation barriers are considerably lower for the $\eta^2(-)$ and $\eta^1$ complexes compared with the $\eta^2(+) complex; the apparent reaction barriers are $E_{app} = 12.1, 0.1$ and -1.5 kJ/mol, respectively, for the $\eta^2(+), \eta^2(-)$ and $\eta^1$ complexes (Figure 5-5 and Table 5-1). Thus, dissociation of the $\eta^2(-)$ and $\eta^1$ complexes will make the predominant contribution to the overall dissociation of
ethane on PdO(101), while adsorption into the less reactive $r^2(\cdot\cdot\cdot)$ state will act to hinder the net dissociation rate.

5.2.5 Micro-kinetic Modeling of C-H Bond Activation for Methane and Ethane on PdO(101)

A micro-kinetic model is used to simulate the dissociation kinetics of methane and ethane on PdO(101) as a function of the surface temperature. The main goals are to estimate the magnitudes and temperature dependence of the initial dissociation probabilities as well as kinetic parameters. A similar model has been employed in chapter 4 to investigate the dissociation kinetics of propane on PdO(101). In the model, it is assumed that an alkane dissociates on PdO(101) by a precursor-mediated mechanism wherein molecularly adsorbed states act as precursors for dissociation and a kinetic competition between desorption and dissociation of the precursors determines the net dissociation probability. DFT-D3 calculations identify one molecularly adsorbed state for methane on PdO(101) and three states for ethane on PdO(101) with similar binding energies. Using the NEB method, it is determined that the chemisorbed states of ethane on PdO(101) must overcome only low energy barriers (< 5 kJ/mol) to interconvert. Thus it is assumed that these states exist in a quasi-equilibrium, as elaborated below. The steps in the kinetic model may be represented by the following equations,

Desorption from state $i$ \[ RH(i) \rightarrow RH(gas) \ [k_{d,i}] \]

Reaction from state $i$ (initial C-H bond cleavage) \[ RH(i) \rightarrow R(i) + H \ [k_{r,i}] \]

Conversion between molecular states \[ RH(i) \rightleftharpoons RH(j) \]
where the symbols $k_{d,i}$ and $k_{r,i}$ represent desorption and reaction rate coefficients, respectively, for molecular state $i$. The total dissociation probability for a particular alkane is given by the following equation,

$$S_t = \frac{\sum y_i k_{r,i}}{\sum y_i (k_{r,i} + k_{d,i})}$$

(5-3)

where $y_i$ represents the probability that the alkane is adsorbed in molecular state $i$.

Because of the assumption that the molecular states exist in a quasi-equilibrium, the $y_i$ values can be equated with equilibrium mole fractions as given by the following equation,

$$y_i = \frac{K_i}{\sum K_i}$$

(5-4)

where $K_i$ is the adsorption equilibrium constant for molecular state $i$ and is computed using parameters determined from the DFT-D3 results.

The rate coefficients for each molecular state are calculated using the following equations derived from transition state theory (TST),

$$k_{d,i}(T) = l_{d,i} \nu_{d,i} e^{-\Delta E_{d,i}^\pm / RT}$$

(5-5)

$$k_{r,i}(T) = l_{r,i} \nu_{r,i} e^{-\Delta E_{r,i}^\pm / RT}$$

(5-6)

where $l_{d,i}$ and $l_{r,i}$ represent statistical factors, $\nu_{d,i}$ and $\nu_{r,i}$ represent the pre-factors and $\Delta E_{d,i}^\pm$ and $\Delta E_{r,i}^\pm$ represent ZPC energy barriers for desorption and reaction of molecular state $i$. The statistical factor for reaction is equal to unity for the $\eta^1$ ethane complex, and two for the methane $\eta^2$ state and the ethane $\eta^2(+) \text{ and } \eta^2(-)$ states. The statistical factor for desorption is equal to unity for each of the molecular states. It is to be noted that
symmetry numbers are omitted from the rotational partition functions when statistical factors (i.e., reaction path degeneracy) are included in the TST formula. The pre-factors for desorption and reaction of molecular state \( i \) are given by the equations,

\[
\nu_{d,i} = \frac{k_B T}{h} \frac{q_{2D} q_r q_{vib(g)}}{q_{ad,i}} \tag{5-7}
\]

\[
\nu_{r,i} = \frac{k_B T}{h} \frac{q_i^*}{q_{ad,i}} \tag{5-8}
\]

where \( q_{2D} \), \( q_r \) and \( q_{vib(g)} \) represent partition functions for two-dimensional (2D) translation, three-dimensional (3D) rotation and intra molecular vibration of a gas-phase molecule and \( q_{ad,i} \) and \( q_i^* \) represent the partition functions for adsorbed state \( i \) and the dissociation transition state for configuration \( i \), respectively. A two-dimensional translational partition function appears in the equation for \( \nu_{d,i} \) because the transition state for desorption is taken as the gas-phase molecule less translational motion perpendicular to the surface. Published moments of inertia of the gas-phase molecules are used to evaluate rotational partition functions. The principal moments of inertia for methane are each equal to 3.17 amu \( \text{Å}^2 \), while the values for ethane are \( I_x = 6.46 \) amu.\( \text{Å}^2 \) and \( I_y = I_z = 25.3 \) amu.\( \text{Å}^2 \). Lastly, \( q_{vib(g)} \) is estimated using the formula for \( 3N - 6 \) uncoupled harmonic oscillators, with vibrational frequencies taken from normal mode analysis applied to the DFT-D3 derived molecular structures.

The pre-factors for desorption depend sensitively on the approximations made in calculating the partition functions of the adsorbed species. The frustrated motions of molecularly adsorbed alkanes tend to be weakly-hindered as evidenced by normal mode vibrational frequencies that are less than about 250 cm\(^{-1} \). As such, modeling the
frustrated motions as harmonic vibrations can significantly underestimate the entropy of an adsorbed alkane and thus overestimate the desorption pre-factor. Recent work by Campbell and Sellers indeed reveals that the entropies of adsorbed molecules are generally much higher than that estimated from harmonic TST. These authors reported a linear correlation between the entropies of adsorbed and gaseous molecules in which the entropy of an adsorbed molecule is equal to about 70% of that of the gaseous molecule for a wide range of molecule-surface combinations. It is shown in chapter 4 that the harmonic model (“3N model”) overestimates the apparent desorption pre-factor \( \nu_d/\nu_r \) of propane on PdO(101) by nearly three orders of magnitude, whereas modeling two of the frustrated modes as free motions (“3N – 2 model”) brings the apparent desorption pre-factor into good agreement with experimental estimates.\(^{109,124}\)

In this section, the kinetic pre-factors and dissociation probabilities computed using so-called 3N and 3N – 2 models for methane and ethane on PdO(101) are compared. In the 3N model, all of the adsorbate motions are treated as harmonic vibrations to compute the partition function, while in the 3N – 2 model a frustrated translation and a frustrated rotation is modeled as free motions while the remaining 3N – 2 motions are modeled as harmonic vibrations. The adsorbate partition function for the 3N – 2 model is given by the following equation,

\[
q_{ad} = q_t^{1D} q_r^{1D} q_{vib}^{3N-2}
\]

(5-9)

where \( q_t^{1D} \) and \( q_r^{1D} \) represent partition functions for free translation and free rotation in one-dimension and \( q_{vib}^{3N-2} \) is the partition function for the remaining 3N – 2 motions modeled as harmonic oscillators. The following equations to compute \( q_t^{1D} \) and \( q_r^{1D} \),
\[ q_t^{1D} = A^{1/2} \left( \frac{2\pi mk_B T}{\hbar^2} \right)^{1/2} \tag{5-10} \]
\[ q_r^{1D} = \left( \frac{8\pi^2 I k_B T}{\hbar^2} \right)^{1/2} \tag{5-11} \]

where \( m \) and \( I \) represent the mass of the alkane molecule and a moment of inertia about an appropriate rotational axis, respectively, and the quantity \( A \) represents the area occupied by an adsorbed alkane molecule at the saturation coverage of the \( \sigma \)-complex state. The partition function for two-dimensional translation \( q_t^{2D} \) is equal to the square of \( q_t^{1D} \).

The frustrated translation along the \textit{cus}-Pd row is modeled as a free translation in one-dimension since the corrugation in this direction is lower than that perpendicular to the \textit{cus}-Pd row. The frustrated rotation that is treated as a free motion corresponds to the rotational mode that involves the smallest changes in the molecule-surface distance. For the methane and ethane \( \eta^2 \) complexes, it is assumed that rotation occurs freely about an axis passing through the center of the Pd-coordinated methyl group and the corresponding \textit{cus}-Pd atom, while for the ethane \( \eta^1 \) complex, it is assumed that free rotation occurs about the C-C bond axis of the ethane molecule. As an approximation, appropriate moments of inertia of the isolated molecules are used when evaluating the 1D rotational partition functions of the adsorbed species. For the \( 3N-2 \) model, it is assumed that the dissociation transition structures execute two free motions on the surface and calculate the partition functions for these motions following the prescriptions described above.

It is instructive to compare the \( 3N \) and \( 3N-2 \) models with analogous models\textsuperscript{93,106} that may be used to obtain bounds on the desorption pre-factors. The \( 3N \) model is a
lattice gas model in which all adsorbate motions are treated as harmonic vibrations. As discussed by Tait et al., an upper bound on the desorption pre-factor may be conveniently obtained from the lattice gas model by assuming that all adsorbate modes of motion are vibrations that remain in the ground state. Such an approximation yields a higher desorption pre-factor than the 3N model because the partition functions for the low-frequency frustrated motions of the adsorbates are included in the calculation of \( \nu_d \) using the 3N model and exceed unity at moderate temperatures. The ideal 2D gas model provides a lower bound on the desorption pre-factor. This model assumes that three modes of adsorbate motion are free, namely, translation in the surface plane (2D) as well as rotation about the surface normal (1D). Compared with the 3N – 2 model, the ideal 2D gas model treats an additional adsorbate mode as a free motion and should thus predict the lower desorption pre-factor.

### 5.2.6 Pre-factors for Alkane Desorption from PdO(101)

Table 5-2 lists average values of the kinetic pre-factors for desorption (\( \nu_d \)) and reaction (\( \nu_r \)) over a temperature range of 150-350 K computed using the 3N and 3N – 2 models for the methane and ethane complexes on PdO(101). The 150-350 K temperature range is selected to facilitate comparison with similar calculations for propane, and note that the pre-factors vary across this temperature range by a maximum of a factor of two for the 3N model and by less than 25% for the 3N – 2 model. As expected, the desorption pre-factors determined using the 3N – 2 model are considerably lower than those calculated using the 3N model (Table 5-2). For the methane complex, the average values of the desorption pre-factor computed using the 3N – 2 vs. 3N model are equal to \( \log(\nu_d) = 14.5 \) and 15.6, respectively, which
corresponds to a difference of about a factor of 12. The desorption pre-factors for the
ethane complex are in the range of \( \log(v_d) = 14.8 \) to 15.5 for the 3\( N-2 \) model and
\( \log(v_d) = 16.3 \) to 16.5 for the 3\( N \) model. The values of \( v_d \) for the ethane complexes are
thus lower by between a factor of about 10 to 30 for the 3\( N-2 \) vs. 3\( N \) models. For
comparison, it is determined that the desorption pre-factors of propane complexes on
PdO(101) are about 100 times lower for the 3\( N-2 \) vs. 3\( N \) models. The reaction pre-
factors are generally higher for the 3\( N-2 \) vs. 3\( N \) models but differ by much less than
the desorption pre-factors (Table 5-2) because the partition functions of both the IS and
TS for dissociation are higher for the 3\( N-2 \) vs. 3\( N \) model. These changes have an
offsetting effect on the computed values of \( v_{r,i} \) (Equation 5-8).

Table 5-2. Average values of the kinetic pre-factors for desorption (\( v_d \)) and reaction
(\( v_r \)) over a temperature range of 150-350 K computed using the 3\( N \) and 3\( N-2 \) models for the methane and ethane complexes on PdO(101).

<table>
<thead>
<tr>
<th>Configuration</th>
<th>3( N ) model</th>
<th>3( N-2 ) model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \log(v_d) )</td>
<td>( \log(v_r) )</td>
</tr>
<tr>
<td>Methane ( \eta^2 )</td>
<td>15.6</td>
<td>12.0</td>
</tr>
<tr>
<td>Ethane ( \eta^2(+) )</td>
<td>16.3</td>
<td>11.9</td>
</tr>
<tr>
<td>Ethane ( \eta^2(-) )</td>
<td>16.5</td>
<td>12.3</td>
</tr>
<tr>
<td>Ethane ( \eta^1 )</td>
<td>16.5</td>
<td>12.1</td>
</tr>
</tbody>
</table>

The desorption pre-factors computed using the 3\( N-2 \) model compare well with
values obtained from the literature. First, the desorption pre-factor predicted by the 3\( N-2 \)
model for methane on PdO(101) agrees quite well with the optimum pre-factor
determined from experimental TPD data;\textsuperscript{79} the values given by the 3\( N-2 \) model vs.
experimental data are \( \log(v_d) = 14.5 \) vs. 14.7, respectively. Unfortunately, experimental
estimates of the desorption pre-factors are unavailable for higher alkanes on PdO(101).
The recently reported Campbell-Sellers equation\textsuperscript{125} has also been used to compute
desorption pre-factors for comparison with the $3N - 2$ model. The Campbell-Sellers equation predicts desorption pre-factors of $\log(\nu_d) = 14.1, 14.7$ and $15.2$ for methane, ethane and propane at the TPD peak temperatures of $130, 167$ and $190$ K for PdO(101), while the corresponding values predicted by the $3N - 2$ model are $\log(\nu_d) = 14.4, 14.8$ to $15.5$ and $15.1$ to $15.5$, respectively. The different configurations of ethane and propane on PdO(101) are responsible for the range of $\nu_d$ values reported for these molecules. The pre-factors determined from the Campbell-Sellers equation agree well with the values determined from the $3N - 2$ model, with the maximum difference equal to a factor of about 7, and are indeed much smaller than the predictions of the $3N$ model. An implication is that the $3N - 2$ model accurately reproduces the entropies of alkanes on PdO(101) at temperatures where the desorption rates are appreciable. The Campbell-Sellers equation slightly underestimates the desorption pre-factors predicted by the $3N - 2$ model for methane and ethane on PdO(101) as well as the value determined experimentally for methane. Further study is needed to determine if these differences are meaningful. Overall, it is concluded that the agreement is quite good between the $3N - 2$ model and the Campbell-Sellers equation for alkanes on PdO(101). This agreement lends confidence to the accuracy of the $3N - 2$ model for describing alkane desorption from PdO(101).

The $3N - 2$ model also predicts values of the apparent desorption pre-factor $(\nu_d/\nu_r)$ that agree well with values determined experimentally for related systems. For example, the apparent desorption pre-factors lie between $50$ to $200$ and $100$ to $400$ for the dissociation of methane and ethane, respectively, on single crystalline Ir surfaces. From the $3N - 2$ model, values of $\nu_d/\nu_r = 222$ for methane and $\nu_d/\nu_r \sim 500$ to $2500$
for ethane on PdO(101) for $T_s = 150$ to 350 K are obtained; the $\nu_d/\nu_r$ values predicted by the $3N$ model are at least an order of magnitude higher (Table 5-2). As shown recently, the $3N - 2$ model reproduces the apparent desorption pre-factor for propane on PdO(101) to within a factor of two.$^{124}$

### 5.2.7 Simulated Dissociation Probabilities

Figure 5-6 A) shows the dissociation probability $S_r$ of methane on PdO(101) as a function of the surface temperature computed using the $3N$ and $3N - 2$ models. As expected, the dissociation probabilities determined from the $3N - 2$ model are higher than those computed using the $3N$ model, with this difference arising primarily from the higher value of the apparent pre-factor for reaction that is predicted by the $3N - 2$ vs. $3N$ model. The zero-point corrected energy barrier for reaction is also lower for the $3N - 2$ model by about 1.2 kJ/mol, which further enhances the dissociation probability predicted by the $3N - 2$ vs. the $3N$ model. The dissociation probability of methane on PdO(101) increases sharply with the surface temperature because the apparent reaction barrier is positive, with values of 14.9 and 16.1 kJ/mol for the $3N - 2$ and $3N$ models, respectively. For the $3N - 2$ model, the dissociation probability of methane on PdO(101) increases from $10^{-5}$ to $1.3 \times 10^{-3}$ as the surface temperature increases from 300 to 1000 K. The dissociation probabilities of methane on PdO(101) that is computed with the $3N - 2$ model are comparable to measured values reported for methane dissociation on Ir(110).$^{127}$
Figure 5-6. Initial dissociation probability of methane and ethane on PdO(101) as a function of the surface temperature, computed using the $3N$ and $3N-2$ kinetic models.

Figure 5-6 B) shows the dissociation probability as a function of surface temperature for ethane on PdO(101) computed using the $3N-2$ and $3N$ models. Similar to the calculations for methane, the $3N-2$ model predicts higher apparent pre-factors for reaction and thus higher dissociation probabilities than the $3N$ model for ethane on PdO(101). The ethane dissociation probabilities predicted by the $3N-2$ vs. $3N$ models differ by a factor of 10 to 20 for surface temperatures above 300 K. From the $3N-2$ model, the dissociation probability of ethane on PdO(101) increases from $6.4 \times 10^{-4}$ to $2.3 \times 10^{-3}$ as the surface temperature increases from 300 to 1000 K.
Dissociation of the ethane $\eta^2(-)$ and $\eta^1$ complexes make the dominant contribution to the total dissociation probability, while dissociation of the ethane $\eta^2(+)\text{ complex makes only a minor contribution. Notice that the dissociation probability is higher for ethane compared with methane at all temperatures, but that the difference decreases with increasing surface temperature. This behavior arises from the stronger temperature dependence of $S_t$ for methane compared with ethane due to the higher, positive value of the apparent reaction barrier for methane on PdO(101).

The computed dissociation probability of ethane on PdO(101) exhibits a qualitatively different dependence on the surface temperature than methane over the range from 100 to 1000 K. For methane, the dissociation probability increases monotonically with increasing surface temperature, whereas the ethane dissociation probability initially decreases as the surface temperature increases, reaching a minimum value at about 275 K, and increases with increasing surface temperature thereafter. This behavior occurs because the apparent reaction barriers are small for the ethane $\eta^2(-)$ and $\eta^1$ complexes (0.1 and -1.5 kJ/mol), and the temperature dependencies of the apparent reaction pre-factors consequently control the temperature dependence of the dissociation probability.

**5.2.8 Temperature Dependence of the Apparent Activation Energy**

The temperature dependence of the apparent reaction pre-factors may be understood by considering limiting behavior. The apparent reaction pre-factor for the $3N - 2$ model may be expressed as,

$$\frac{v_r}{v_d} = \frac{(q_t^1 q_r^1 q_{vib}^{3N-3})^*}{(q_t^{2D} q_r^{3D} q_{vib}^{3N-6})_{gas}}$$

(5-12)
At low temperature, the vibrational contribution to the apparent pre-factor varies relatively weakly with surface temperature, whereas each degree of freedom for a free motion contributes a factor of $T^{1/2}$. Based on the contributions made by free motions, the apparent reaction pre-factor for the $3N - 2$ model scales approximately as $T^{3/2}$ in the low temperature limit, and will thus initially decrease with increasing surface temperature. At sufficiently high temperature, the vibrational motions behave classically and the partition function for each harmonic oscillator scales with $T$. The apparent reaction pre-factor for the $3N - 2$ model thus scales with $T^{3/2}$ in the high temperature, classical limit. The crossover between the limiting behaviors occurs at relatively low temperature because the frustrated vibrations of the adsorbed species are characterized by low frequencies, between 100 and 230 cm$^{-1}$ for the ethane complexes.

Apparent activation energies have been computed to further quantify the temperature dependence of the dissociation probabilities, where the apparent activation energy for reaction is defined as proportional to the instantaneous slope of an Arrhenius plot of $S_r$ vs. $T$ as given by the following equation,

$$E_A = RT^2 \frac{d\ln S_r}{dT} \quad (5-13)$$

Figure 5-7 shows the apparent activation energies as a function of the surface temperature computed using the results of the $3N - 2$ model for the dissociation of methane and ethane on PdO(101). The apparent activation energy for methane increases from 13.5 to 26.0 kJ/mol as the surface temperature increases from 175 to 1000 K, though $E_A$ first exhibits a slight decrease with temperature from 100 to 175 K.
Figure 5-7. Apparent activation energies evaluated using the $3N-2$ model, plotted as a function of the surface temperature for methane and ethane on PdO(101).

The apparent activation energy for ethane dissociation on PdO(101) increases from -2.5 to 14.7 kJ/mol as the surface temperature increases from 100 to 1000 K, with the activation energy first becoming positive at a temperature of 273 K. This analysis demonstrates that the apparent activation energies for methane and ethane dissociation on PdO(101) generally increase with increasing surface temperature, causing the dissociation probabilities to become more strongly dependent on the surface temperature once the apparent activation energy becomes positive. This behavior should be general for the precursor-mediated dissociation of adsorbed molecules as it originates from the entropic contributions to the dissociation probability, as discussed above.

Lastly, it is noted that the apparent activation energies determined from the $3N-2$ model increase by about 13 to 18 kJ/mol for surface temperatures increasing from
100 to 1000 K. While relatively small, this energy range does represent a significant fraction of the apparent reaction barriers for methane and ethane dissociation on PdO(101) computed using DFT-D3 (Table 5-2). It is thus important to consider the temperatures at which activation energies for alkane dissociation are measured when making comparisons among datasets. For example, Seets et al. report an apparent activation energy of ~21 kJ/mol for the trapping-mediated dissociation of methane on Ir(110) at surface temperatures between 900 and 1100 K. For this same temperature range, an average value of 26 kJ/mol is predicted for the apparent activation energy for methane dissociation on PdO(101), which suggests that Ir(110) is slightly more reactive than PdO(101) toward methane dissociation. The apparent activation energy estimated for temperatures between 900 and 1100 K is considerably higher than the value of the ZPC apparent reaction barrier (16.1 kJ/mol) for methane on PdO(101), thus demonstrating the importance of taking into account the temperature dependence of the apparent activation energy.

5.3 Summary

Both conventional DFT and dispersion-corrected DFT-D3 calculations have been to investigate pathways for the initial C-H bond cleavage of methane and ethane σ-complexes adsorbed on the PdO(101) surface. It is found that dispersion interactions cause a nearly constant downshift in the energy levels of each stationary state along a given reaction pathway. As as result, DFT-D3 predicts lower and more physically realistic energy barriers for alkane C-H bond scission relative to the gas-phase reference, while giving nearly the same energy differences between stationary states as predicted by conventional DFT for a given reaction pathway. Using DFT-D3, it is found
that the barriers for C-H bond activation of a CH$_4$ $\eta^2$ complex on PdO(101) are 55.2 and
16.1 kJ/mol relative to the adsorbed and gaseous states, respectively. It is also
determined that dehydrogenation of the resulting CH$_3$-Pd$_{\text{cus}}$ species as well as
conversion to a CH$_3$O$_{\text{cus}}$ species are significantly more energetically demanding than
initial CH$_4$ activation on PdO(101). Among the three stable ethane $\sigma$-complexes on
PdO(101) that were identified, DFT-D3 predicts that an $\eta^2$ and an $\eta^1$ ethane complex
can each undergo C-H bond cleavage with intrinsic barriers that are similar to that for
activation of the CH$_4$ $\eta^2$ complex but with apparent barriers close to zero.

Micro-kinetic models based on transition state theory are also used to simulate
the dissociation kinetics of methane and ethane on PdO(101). It is shown that the so-
called $3N-2$ model, in which two frustrated adsorbate motions are modeled as free
motions, predicts desorption pre-factors that agree well with both experimental
estimates and the predictions of a correlation reported by Campbell and Sellers.$^{125}$ The
desorption pre-factors determined from the $3N-2$ model for methane and ethane on
PdO(101) are at least ten times smaller than the desorption pre-factors predicted by a
model in which all adsorbate motions are treated as harmonic oscillators. The
dissociation probabilities scale with the apparent pre-factors for reaction and thus also
differ by at least factor of ten for the $3N-2$ vs. $3N$ models. Lastly, how the apparent
reaction pre-factor influences the temperature dependence of the alkane dissociation
probabilities is discussed, and it is shown that this dependence gives rise to an
apparent activation energy that generally increases with increasing surface
temperature. Overall, the micro-kinetic simulations reveal the importance of accurately
describing the entropic contributions in calculations of alkane dissociation kinetics, and
show that the $3N - 2$ model represents a significant improvement in accuracy over harmonic TST for alkane-surface systems.
The surface chemistry of late transition-metal oxides is central to many applications of oxidation catalysis, including the catalytic combustion of natural gas, exhaust gas remediation in automobiles and fuel cell catalysis. Under oxygen-rich conditions, various types of oxides phases can develop on transition metal surfaces which can cause significant changes in catalytic behavior. Of particular relevance to the present study are reports that bulk-like PdO is highly active toward the completion oxidation of methane and that the formation of PdO is responsible for the favorable performance of Pd as an oxidation catalyst under oxygen-rich conditions. Investigations with supported Pd-catalysts also demonstrate that the combustion products can have deleterious effects on the catalytic activity, which motivates further study of the adsorption of CO\textsubscript{2} and H\textsubscript{2}O on PdO surfaces.

Studies of the surface chemistry of a high-quality PdO(101) thin film on Pd(111) describe that the complete oxidation of \textit{n}-alkanes (> C\textsubscript{2}) is facile on this PdO surface, with initial C-H bond cleavage occurring below 200 K. An implication of these findings is that the PdO(101) surface is representative of active surfaces which develop on supported-Pd catalysts in oxidizing environments. Investigations of the surface chemistry of PdO(101) thus have potential to provide fundamental insights into applications of Pd-catalyzed oxidation chemistry. In this chapter, investigations on PdO(101) are extended to the adsorption of CO\textsubscript{2} in an effort to further clarify the binding
of small molecules on this surface.

The adsorption characteristics of CO$_2$ on well-defined transition-metal oxides share common features among the systems that have been investigated in detail. For example, experiments using temperature programmed desorption (TPD) commonly reveal multiple CO$_2$ desorption peaks below 200 K arising from physisorbed and weakly-bound chemisorbed species.$^{133-137}$ Characterization using surface vibrational spectroscopy has provided detailed information about the nature of CO$_2$ adsorbed on oxide surfaces. For example, vibrational spectra obtained from CO$_2$ adsorbed on both TiO$_2$(110)$^{133}$ and Cr$_2$O$_3$(0001)$^{134}$ reveal that the weakly-bound adsorbates remain in linear geometries, implying limited charge transfer between the molecules and the surface. CO$_2$ also adsorbs on Cr$_2$O$_3$(0001) as a carboxylate species (CO$_2$$^{\delta-}$) and achieves stronger binding to the surface compared with the linear species. The carboxylate species constitute a significant fraction of the CO$_2$ desorption yield from Cr$_2$O$_3$(0001) and remain stable to above room temperature.

Investigations with RuO$_2$(110) also report weakly-bound adsorbed states of CO$_2$ that desorb below 200 K during TPD as well as a small fraction of CO$_2$ which desorbs at 315 K.$^{135, 136}$ In this case, vibrational spectroscopy reveals that two CO$_2$ desorption features between 175 and 190 K arise from a chemisorbed CO$_2$$^{\delta-}$ species and CO$_2$:CO$_2$$^{\delta-}$ dimers. The carboxylate species which form on RuO$_2$(110)$^{135}$ are bound more weakly than carboxylate on Cr$_2$O$_3$(0001)$^{134}$ and exhibit binding energies that are comparable to those of the linear CO$_2$ species identified on TiO$_2$(110).$^{133, 137}$ The CO$_2$ desorption feature at 315 K obtained from RuO$_2$(110) has been attributed to a carbonate species,$^{135, 136}$ in good agreement with computational predictions.$^{138}$
contrast, only small quantities of carbonate have been observed following CO$_2$ adsorption on TiO$_2$(110)$^{133}$ and carbonate formation was not observed on Cr$_2$O$_3$(0001) in the work of Seiferth et al.$^{134}$ Taken together, these prior studies demonstrate that similar configurations of adsorbed CO$_2$ can exhibit wide variations in binding energies among different transition-metal oxides and that the tendency for carbonate formation depends strongly on the nature of the oxide surface.

Described in this chapter is the adsorption of CO$_2$ on a PdO(101) surface investigated using both TPD experiments and dispersion-corrected DFT-D3 calculations. It is observed that CO$_2$ prefers to adsorb on the cus-Pd row as dimers and trimers, and begins to physisorb on the 4f-Pd sites after the cus-Pd row saturates. The DFT-D3 predictions are seen to agree well with experimental estimates of the binding energies and saturation coverages of CO$_2$ adsorbed on the cus-Pd and 4f-Pd sites of PdO(101). The good quantitative agreement between experiment and computation demonstrates that the DFT-D3 method is capable of accurately describing coverage effects in molecular adsorption.

6.2 Computational Details

The dispersion-corrected DFT (DFT-D3) calculations presented are performed using the Vienna ab initio simulation package (VASP)$^{84-87}$ integrated with the recently-reported ‘D3’ method of treating dispersion in DFT calculations as developed by Grimme and coworkers.$^{48}$ In the DFT-D3 method, dispersion forces and energies ($F_{disp}, E_{disp}$) are empirically determined and added to the ionic forces ($F_{dft}$) and energy ($E_{dft}$) determined by conventional DFT. Initial calculations show that DFT-D3 provides a more accurate description of molecular adsorption on metal surfaces than the earlier
DFT-D1 and D2 methods. Key improvements included in the DFT-D3 method are more accurate estimates of the $C_6$ parameters from time-dependent DFT calculations, and the use of fractional coordination numbers to allow the $C_6$ parameters to vary with the local chemical environment.

Projector augmented wave (PAW) pseudopotentials provided in the VASP database and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional are used with a plane wave cutoff of 400 eV to determine $F_{dft}$ and $E_{dft}$ in these calculations. Parameters for the calculations are similar to those used in earlier studies of the PdO(101) surface. Calculation of $E_{dft}$ is done using a residual minimization method with direct inversion in the iterative subspace for electronic relaxations accelerated using Methfessel-Paxton Fermi-level smearing with a Gaussian width of 0.1 eV. The dispersion energy $E_{disp}$ is determined using Equation 6-1 where the pairwise interactions are summed over all of the atoms located within a cutoff radius of 50 Å. The additive term ($E_{disp}$) is a function of $n^{th}$ order inter-nuclear distances ($r_{AB}^{-n}$), dispersion coefficients ($C_{nAB}^{AB}$) that have been computed ab initio by time dependent DFT, a scaling factor ($s_n$) that ensures asymptotic exactness, and a damping function ($f_{d,n}(r)$). These parameters have been directly taken from the recent implementation of dispersion in DFT calculations by Grimme et al.

$$E_{disp} = -\frac{1}{2} \sum_{AB} \left[ s_6 \frac{C_6^{AB}}{r_6^{AB}} f_{d,6}(r_{AB}) + s_8 \frac{C_8^{AB}}{r_8^{AB}} f_{d,8}(r_{AB}) \right]$$  (6-1)
The total ionic forces ($F_{dft} + F_{disp}$) are relaxed using a limited memory Broyden-Fletcher-Goldfarb-Shanno optimization method\textsuperscript{59} until the forces on all unconstrained atoms are less than 0.03 eV/Å.

Figure 6-1 illustrates the stoichiometric PdO(101) surface that is investigated in this study. Bulk crystalline PdO has a tetragonal unit cell and consists of square planar units of Pd atoms fourfold coordinated with oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit cell, where the $\bar{a}$ and $\bar{b}$ lattice vectors coincide with the [010] and [$\overline{1}01$] directions of the PdO crystal, respectively. The stoichiometric PdO(101) surface consists of alternating rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the $\bar{a}$ direction shown in Figure 6-1.

![Figure 6-1](image)

**Figure 6-1.** Model representation of the stoichiometric PdO(101) surface. Coordinatively saturated (4f) and coordinatively unsaturated (cus) Pd and O atoms have been labelled. The $\bar{a}$ and $\bar{b}$ directions correspond to the [010] and [$\overline{1}01$] crystallographic directions of bulk PdO.
Thus, half of the surface O and Pd atoms are coordinatively unsaturated (cus). The side view of PdO(101) shows that the coordinative environment associated with each cus-Pd atom resembles a square planar Pd complex with a coordination vacancy directed away from the surface and three oxygen ligands, one of which is a cus-O atom. The areal density of each type of coordinatively-distinct atom of the PdO(101) surface is equal to 35% of the atomic density of the Pd(111) surface. Hence, the coverage of cus-Pd atoms is equal to 0.35 ML, and each PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms.

The PdO(101) model used in the computational study is the same as that used in earlier studies and consists of four layers corresponding to a thickness of ~9 Å. Earlier work has shown that this thickness is sufficient to accurately model the experimental PdO(101) film on Pd(111). The PdO(101) slab is strained to match the structure reported by LEED experiments\textsuperscript{19,20} ($\bar{a} = 3.057$ Å, $\bar{b} = 6.352$ Å). A vacuum spacing of 20 Å is maintained normal to the surface and a $4 \times 2 \times 1$ (2×4×1) Monkhorst-Pack $k$-point mesh has been used for the $1 \times 4$ (2×2) cell size. Finer mesh sizes or increasing the number of layers does not result in significant changes in the adsorption energy (< 0.1 kJ/mol). The adsorption/binding energy ($E_{ads}$) is defined as the difference between the sum of total energies for the isolated molecule ($E_{iso}$) and bare surface ($E_{bare}$) with that of the chemisorbed molecule/surface system ($E_{chemisorb}$) as seen in Equation 6-2.

$$E_{ads} = [E_{bare} + E_{iso}] - E_{chemisorb}$$ (6-2)

Normal mode analysis have been performed to ensure that the relaxed configurations of CO$_2$ on PdO(101) possess only real vibrational frequencies and are
thus true minima. The vibrational modes are calculated by fixing the surface atoms while leaving the chemisorbed molecule unconstrained.

6.3 Results and Discussion

6.3.1 Experimental Observation

Temperature programmed desorption (TPD) spectra for CO$_2$ (shown in Figure 6-2) displays two desorption features, a sharp high temperature $\varepsilon_1$ peak centered at 179 K and a low temperature $\varepsilon_2$ peak centered at $\sim$132 K that broadens and downshifts to $\sim$112K while growing sharply as CO$_2$ coverage increases above $\sim$0.19ML. The appearance of this broad desorption region suggests the CO$_2$ molecule begins to encounter a more diverse range of local binding environments after the $\varepsilon_1$ states saturates. A similar trend is observed for CO$_2$ desorption from RuO$_2$(110). Comparison of the CO$_2$ TPD spectra obtained from PdO(101) vs RuO$_2$(110) suggests that $\varepsilon_1$ states correspond to chemisorbed states while $\varepsilon_2$ states correspond to physisorbed states. The overall average desorption activation energies for $\varepsilon_1$ adsorbed states is estimated to be 54 ± 8 kJ/mol while that for $\varepsilon_2$ states is estimated to be 37 ± 5 kJ/mol. Saturation coverage of CO$_2$ on PdO(101) is 0.47ML which corresponds to 67% of the total Pd site density of 0.70 ML. The nearly even distribution of CO$_2$ population between $\varepsilon_1$ and $\varepsilon_2$ states suggest the possibility that these states correspond to CO$_2$ bound on cus-Pd and 4f-Pd sites respectively.

Earlier experimental studies$^{96}$ illustrated that preadsorbed $^{18}$O$_2$ effectively blocks H$_2$ and n-butane adsorption onto cus-Pd sites of PdO(101). Based on this notion, TPD experiments involving preadsorption of $^{18}$O$_2$ is seen to impede CO$_2$ adsorption into the $\varepsilon_1$ states while having a smaller influence on CO$_2$ bound in the $\varepsilon_2$ state. Thus
preadsorbed O2 is seen to selectively block CO₂ adsorption into the ε₁ state. This further confirms that the more strongly-bound ε₁ states corresponds to CO₂ molecules that coordinate with the cus-Pd sites.

Figure 6-2. CO₂ TPD spectra obtained after adsorbing CO₂ on PdO(101) at 85 K. A constant heating rate of 1 K s⁻¹ was used in each measurement.

6.3.2 DFT-D3 Predictions of CO₂ Binding Configurations on PdO(101)

DFT-D3 is used to identify stable configurations of CO₂ adsorbed on PdO(101), and characterize how the structure of the CO₂ layer evolves with increasing coverage. Several configurations of isolated CO₂ molecules on PdO(101) were explored and it was found that CO₂ maximizes its binding energy by interacting with the cus-Pd row of the PdO(101) surface. Specifically, DFT-D3 predicts that CO₂ achieves binding energies of 32.6 and 40.3 kJ/mol, respectively, by adsorbing in the bent vs. linear configurations shown in Figure 6-3. DFT-D3 identifies other stable configurations for CO₂ adsorbed on
the *cus*-Pd and the *4f*-Pd row (not shown), but the binding energies are lower (< 24 kJ/mol) than those in the preferred bent and linear configurations of CO$_2$ adsorbed on the *cus*-Pd row.

In the most favored configuration, the CO$_2$ molecule remains linear and adopts an end-on binding geometry wherein the molecule leans toward the *cus*-O atom row and one of its O-atoms lies close to a *cus*-Pd atom (Figure 6-3 A)). The linear CO$_2$ adsorbate experiences only slight C-O bond elongation from the gas-phase value of 1.15 Å. The length of the C-O bond closest (farthest) from the *cus*-Pd atom is 1.19 (1.16) Å and the bond angle is 178°. Analysis predicts that electronic interactions account for 19.3 kJ/mol (~48%) of the total binding energy of the linear configuration, with molecule-surface dispersion interactions accounting for the remainder. Electrostatic
interactions appear to dominate the contribution to the electronic interaction energy of
the linear configuration of CO$_2$ on the PdO(101) surface. According to Bader charge
analysis, the charges on the C and O atoms of the linearly adsorbed CO$_2$ molecule are
+4.0 and -2.0, respectively. Thus, the CO$_2$ molecule is neutral in the linear configuration,
as expected, but each C-O bond is highly polarized. Bader analysis also predicts
charges of +0.76 and -0.87 for the cus-Pd and cus-O atoms of the PdO(101) surface. In
the linear binding configuration, the CO$_2$ molecule is positioned in a way that would
produce favorable Coulombic interactions with the surface since an O-atom of the CO$_2$
molecule lies close to a cus-Pd atom while the C-atom is close to the neighboring cus-O
atom. Furthermore, Bader analysis predicts negligible charge transfer between the
molecule and surface when CO$_2$ adopts the linear configuration. An implication is that
dative bonding with the surface is relatively weak for the linear CO$_2$ configuration.

CO$_2$ can also bind relatively strongly on PdO(101) by adopting a bent
configuration along the cus-Pd row, i.e., a carboxylate species (Figure 6-3 B)). This bent
CO$_2$ configuration is analogous to an $\mu_2$-$\eta^2$ bonding configuration$^{139}$ wherein an O-atom
and the C-atom of the CO$_2$ molecule coordinate with different cus-Pd atoms, resulting in
a side-on binding geometry. Bader analysis predicts that the surface transfers 0.36
electrons to the CO$_2$ molecule in the side-on geometry, causing the adsorbed CO$_2$
molecule to bend and the C-O bonds to elongate. The CO$_2$ bond angle is equal to 136$^\circ$
for the bent configuration and the C-O bond length is equal to 1.27 Å (1.22 Å) for the
bond closest (farthest) from the cus-Pd row. It is found that electronic interactions
contribute only 5.4 kJ/mol (< 17%) to the total binding energy for the bent CO$_2$ species
on PdO(101), with dispersion interactions making the dominant contribution. Thus, even
though charge transfer is significant when CO$_2$ adopts the bent configuration, the resulting electronic interactions between the molecule and the surface make only a small contribution to the total binding energy.

Attempts were also made to adsorb CO$_2$ directly on top of a $cus$-Pd atom to determine if the molecule would adopt $\eta^1$ and $\eta^2$ configurations that are analogous to those reported for mononuclear transition-metal CO$_2$ complexes.\textsuperscript{139} For these cases, the CO$_2$ molecule relaxes to a linear configuration that lies along the $cus$-Pd row and achieves a binding energy of 22 kJ/mol, which is lower than the energies of the stable configurations shown in Figure 6-3. A facile pathway for the formation of a surface CO$_3$ species by reaction between CO$_2$ and the $cus$-O atoms was not identified, which is consistent with experimental observations. These calculations provide further support for concluding that the linear and bent configurations shown in Figure 6-3 are the preferred binding configurations of isolated CO$_2$ molecules on PdO(101).

**6.3.3 Evolution of CO$_2$ Binding Configurations on PdO(101) with Increasing Coverage**

DFT-D3 is used to investigate how the molecular configurations within the CO$_2$ layer evolve with increasing coverage on PdO(101). Since a $1 \times 4$ supercell is used to model the PdO(101) surface, the addition of a single CO$_2$ molecule to the supercell is equivalent to increasing the CO$_2$ coverage by 0.087 ML. In the calculations, the CO$_2$ coverage is increased in 0.087 ML steps and multiple configurations are explored in an attempt to identify the global minimum at each coverage. CO$_2$ coverages from 0.087 to 0.52 ML are investigated which corresponds to a range of one to six CO$_2$ molecules in the $1 \times 4$ supercell. Figure 6-4 shows representative configurations that were investigated and highlights the energetically preferred pathway for the adsorbed layer.
as a function of the CO\textsubscript{2} coverage. The energy value shown underneath each configuration is equal to the binding energy per CO\textsubscript{2} molecule, while the energy value shown above (or below) an arrow connecting different configurations represents the energy change upon adsorption, which is defined as the energy difference between the final configuration and the initial configuration plus a gas-phase CO\textsubscript{2} molecule.

The DFT-D3 calculations predict that CO\textsubscript{2} molecules have a tendency to adsorb on PdO(101) as “mixed” pairs, consisting of a linear and a bent CO\textsubscript{2} molecule occupying adjacent sites along the \textit{cus}-Pd row. As mentioned above, a single CO\textsubscript{2} molecule adsorbed in the linear configuration on PdO(101) achieves a binding energy of 40.3 kJ/mol. Adsorption of a second CO\textsubscript{2} molecule into the linear configuration (Figure 6-4), which raises the total CO\textsubscript{2} coverage to 0.17 ML, produces a slightly smaller energy change of about 36.8 kJ/mol. Notice that linear CO\textsubscript{2} molecules adsorbed on adjacent sites rotate away from one another, indicating that these species repel (Figure 6-4). In contrast, adsorbing a second CO\textsubscript{2} molecule in a bent configuration causes the original linear CO\textsubscript{2} molecule to rotate toward the bent molecule due to attractive interactions between these species.

The electrostatic attraction between the linear and bent CO\textsubscript{2} molecules arises from strong polarization of the C-O bonds. The corresponding energy change for generating the more favored of two possible linear-bent CO\textsubscript{2} pairs is 44.4 kJ/mol, which is 7.6 kJ/mol more exothermic than adsorbing the second CO\textsubscript{2} molecule in a linear configuration. The structure of the linear-bent CO\textsubscript{2} pair on PdO(101) is analogous to that of a CO\textsubscript{2}:CO\textsubscript{2}\textsuperscript{δ−} dimer, though the O---C bond distance between the linear and bent
CO$_2$ species is greater than that reported for the gas-phase CO$_2$:CO$_2$$^-$ dimer$^{140}$ (2.93 Å vs. 2.40 Å).
Figure 6-4. Stable configurations of CO$_2$ on PdO(101) as a function of CO$_2$ coverage predicted by DFT-D3. The minimum energy pathway based on the heats of adsorption is highlighted by orange arrows. The energy value shown underneath each image represents the binding energy per CO$_2$ molecule for the configuration. The energy value shown below (or above) each arrow represents the heat of adsorption as defined in the text. All energies are given in units of kJ/mol.
Recall that the formation of CO$_2$:CO$_2^{5-}$ dimers has been reported for CO$_2$ adsorbed on the RuO$_2$(110) surface.$^{135}$ The DFT-D3 calculations predict that CO$_2$ pair configurations also form on the PdO(101) surface because CO$_2$ can achieve favorable binding in both a neutral (linear) and an anionic (bent) configuration on the cus-Pd row and that these species interact favorably with one another.

The DFT-D3 calculations predict that CO$_2$ continues to adsorb into stable configurations on the cus-Pd row as the CO$_2$ coverage increases to 0.26 ML. The favored configuration at 0.26 ML corresponds to a linear-bent-linear combination of CO$_2$ molecules which forms as a third CO$_2$ molecule adsorbs on the cus-Pd site adjacent to the linear-bent CO$_2$ pair. The corresponding energy change for the formation of the linear-bent-linear combination is equal to 46.6 kJ/mol, which is similar to the energy change for the formation of the linear-bent CO$_2$ pair. The three CO$_2$ molecules of the linear-bent-linear combination occupy four cus-Pd sites, and effectively saturate the cus-Pd row. CO$_2$ can achieve a coverage of 0.35 ML on the cus-Pd row if each of the molecules adopts the linear configuration and adsorbs on adjacent sites (Figure 6-4). However, DFT-D3 predicts that this all-linear configuration is unfavorable. For example, transformation of the linear-bent-linear configuration at 0.26 ML to the all-linear configuration at 0.35 ML via CO$_2$ adsorption is endothermic by 17 kJ/mol. Electrostatic repulsion between the CO$_2$ molecules is responsible for the low stability of the all-linear configuration. The favored linear-bent-linear configuration is preserved when the fourth CO$_2$ molecule adsorbs on the 4f-Pd row. The corresponding energy change of adsorption is equal to 33.9 kJ/mol, which is significantly more favorable than formation of the all-linear configuration on the cus-Pd row. The DFT-D3 calculations thus predict
that CO$_2$ molecules will saturate the \textit{cus}-Pd row of PdO(101) at a coverage near \(~0.26\) ML, which agrees well with experimental estimate of \(~0.22\) ML for the maximum coverage of CO$_2$ molecules adsorbed in the $\varepsilon_1$ state.

CO$_2$ molecules adsorb on the 4$f$-Pd sites of the PdO(101) surface as the coverage increases from 0.26 to 0.52 ML, with the energy of adsorption decreasing from 33.9 to 28.9 kJ/mol. Dispersion interactions dominate the binding of CO$_2$ on the 4$f$-Pd sites, thus demonstrating that CO$_2$ on the 4$f$-Pd sites is a physisorbed species. For a single CO$_2$ molecule adsorbed on the 4$f$-Pd row, it is determined that electronic interactions are slightly repulsive and that dispersion is solely responsible for the molecule-surface binding. It is noted that CO$_2$ adsorption onto the 4$f$-Pd sites causes changes in the geometries of CO$_2$ molecules adsorbed on the \textit{cus}-Pd row. For example, one of the linear CO$_2$ molecules on the \textit{cus}-Pd row adopts a more upright geometry after a second CO$_2$ molecule adsorbs on the 4$f$-Pd row to raise the total coverage from 0.35 to 0.44 ML (Figure 6-4). This finding highlights the fact that the structure of the entire CO$_2$ layer adjusts to accommodate the CO$_2$ molecules that adsorb at high coverages. According to DFT-D3, increasing the CO$_2$ coverage to 0.61 ML is energetically unfavorable due to crowding within the adsorbed layer. The calculations thus suggest that the CO$_2$ layer on PdO(101) saturates at a coverage near 0.52 ML, in good agreement with experimental estimate of 0.47 ML. The favorable comparisons between the computational and the experimental results support the conclusion that the $\varepsilon_2$ TPD feature arises from CO$_2$ molecules adsorbed on the 4$f$-Pd sites of PdO(101).
Transition-state theory formula is used to calculate desorption pre-factors for several of the stable CO\(_2\) species predicted by DFT-D3. According to transition-state theory, the desorption pre-factor is given by the equation,

\[
\nu_d = \frac{k_B T q_{TS}}{h q_{ad}}
\]  

(6-2)

where \(q_{ad}\) and \(q_{TS}\) represent the partition functions of the adsorbed state and the transition state, respectively, and the transition state is taken as a gas-phase CO\(_2\) molecule less one degree of translational freedom. Using the vibrational frequencies computed for a gaseous CO\(_2\) molecule and several adsorbed CO\(_2\) species predicted by DFT-D3, desorption pre-factors of \(~10^{16}\) and \(10^{17}\) s\(^{-1}\) are estimated for the linear and bent CO\(_2\) configurations on the \textit{cus}-Pd row of PdO(101) (Figure 6-3), respectively. Similar pre-factors are predicted for CO\(_2\) desorption from the dimer configurations which form at 0.17 ML. The computed pre-factors of \(10^{16}\) and \(10^{17}\) s\(^{-1}\) lie on the high end of the range of values discussed above, demonstrating that CO\(_2\) molecules adsorbed on the \textit{cus}-Pd sites are rather constrained. Analysis of the measured \(\varepsilon_1\) TPD peak of CO\(_2\) yields average binding energies of 55 and 59 kJ/mol when the desorption pre-factor is taken as \(10^{16}\) vs. \(10^{17}\) s\(^{-1}\), respectively. Thus, the predicted energy change for CO\(_2\) adsorption on the \textit{cus}-Pd sites (\(~43\) kJ/mol) agrees to within about 25% (\(~14\) kJ/mol) of the experimental estimate of the binding energy of CO\(_2\) in the \(\varepsilon_1\) state (\(~57\) kJ/mol) for the range of desorption pre-factors that is suggested by the DFT-D3 results. Similarly, a desorption pre-factor of \(3 \times 10^{14}\) s\(^{-1}\) is calculated for a single CO\(_2\) molecule physisorbed on the \(4f\)-Pd row and estimate an average binding energy of 36 kJ/mol for CO\(_2\) desorbing in the \(\varepsilon_2\) TPD peak when the pre-factor is set equal to \(3 \times 10^{14}\) s\(^{-1}\) in the TPD
analysis. According to DFT-D3, the average binding energy of CO$_2$ physisorbed on the 4f-Pd sites of PdO(101) is $\sim$32 kJ/mol, which agrees to within better than 15% ($\sim$4 kJ/mol) of the experimental estimate.

Thus the experimental and computational results provide a consistent description of the evolution of the CO$_2$ layer on PdO(101) with increasing coverage. The results demonstrate that CO$_2$ adsorbs initially on the cus-Pd row and then physisorbs on the 4f-Pd row, with the CO$_2$ molecules distributed evenly between these states at saturation of the adsorbed layer. The experimental and computed binding energies also agree well, demonstrating that the DFT-D3 calculations accurately take into account dispersion interactions in the CO$_2$/PdO(101) system. It is noted that the average binding energy of CO$_2$ on the cus-Pd row is higher than that of the CH$_4$ $\sigma$-complex which acts as a precursor for initial C-H bond activation on PdO(101) ($\sim$54 vs. 41 kJ/mol).$^{79,96}$ This difference suggests that CO$_2$ adsorption on the cus-Pd sites can hinder the adsorption and activation of CH$_4$ on PdO(101), which is consistent with reports that CO$_2$ acts as a mild poison in the catalytic combustion of methane by Pd.$^{130,131}$ Indeed, it has been found that pre-adsorbing H$_2$O on the cus-Pd sites completely suppresses the formation of alkane $\sigma$-complexes and the subsequent activation and oxidation of alkanes on PdO(101), which is also consistent with reports that water acts as a strong poison in Pd-catalyzed methane oxidation.$^{132}$ Future experiments of CO$_2$ and CH$_4$ co-adsorption should help to clarify the possibility that pre-adsorbed CO$_2$ suppresses the formation of CH$_4$ $\sigma$-complexes on PdO(101).

According to DFT-D3, the formation of CO$_2$:CO$_2$$^\delta+$ dimers and CO$_2$:CO$_2$$^\delta+$:CO$_2$ trimers stabilizes the CO$_2$ molecules adsorbed on the cus-Pd row. These aggregates are likely
to form on PdO(101) at low coverage to an extent that depends on the surface mobility of the CO$_2$ adsorbates. It has been previously found that the formation of HO-H$_2$O dimers and mixed trimers is favorable during H$_2$O adsorption on PdO(101).$^{58}$ For both CO$_2$ and H$_2$O, electron transfer from the cus-Pd atoms to the adsorbed species produces negatively-charged adsorbates that experience attractive interactions with co-existing neutral adsorbates. The calculations thus show that molecule-surface charge exchange mediates the formation of stable aggregates of CO$_2$ and H$_2$O on PdO(101). Clustering of other Lewis acidic adsorbates may also occur on PdO(101) and is important to understand because such clustering could have marked effects on the reactivity of adsorbed species.

6.4 Summary

The adsorption of CO$_2$ on PdO(101) has been investigated using TPD experiments and DFT-D3 calculations. It is found that CO$_2$ desorbs from PdO(101) in two main TPD peaks ($\varepsilon_1$ and $\varepsilon_2$) centered at ~176 and 120 K, with these states populating nearly sequentially with increasing coverage. The $\varepsilon_1$ and $\varepsilon_2$ states saturate at CO$_2$ coverages of ~0.22 and 0.25 ML, respectively, and have average binding energies of 54 ± 8 and 37 ± 5 kJ/mol. Experiments of CO$_2$ adsorption on pre-adsorbed O$_2$ and H$_2$O layers provide evidence that the $\varepsilon_1$ and $\varepsilon_2$ states correspond to CO$_2$ molecules adsorbed on the cus-Pd and 4f-Pd sites of PdO(101), respectively. Neither carbonate nor bicarbonate species appear to form on PdO(101) under the conditions studied.

Calculations using the dispersion-corrected DFT-D3 method provide excellent agreement with experimental results. The calculations predict the same CO$_2$ binding
sites as suggested by the co-adsorption experiments, and predict saturation coverages and CO₂ binding energies that agree well with experimental estimates. From the calculations, it is determined that CO₂ prefers to initially adsorb on the *cus*-Pd row of PdO(101) by adopting a linear configuration in which the molecular axis is perpendicular to the *cus*-Pd row. The calculations further predict that CO₂ molecules have a tendency to form linear-bent pairs and linear-bent-linear trimers along the *cus*-Pd row, the pairs adopting a structure which resembles that of the T-shaped, gas-phase CO₂:CO₂^5- dimer. CO₂ begins to physisorb on the 4f-Pd sites as the coverage increases above 0.26 ML, and effectively saturates these sites when the total coverage reaches 0.52 ML. The good agreement between experimental and computational results lends confidence in the ability of the DFT-D3 method to accurately predict coverage effects in the adsorption of small molecules on transition metal oxide surfaces.
CHAPTER 7
CONCLUSIONS

Ab initio quantum mechanical calculations based on density functional theory have been used to examine the chemisorption and activity of various molecular species on PdO(101). Calculations predict that \( n \)-alkanes bind more strongly on PdO(101) than on Pd(111), and that the desorption energies scale linearly with alkane chain length on both surfaces. Alkane interaction on these surfaces can be decomposed into dispersion and electronic components. Though dispersion energies are similar in magnitude for a given \( n \)-alkane on Pd(111) and PdO(101), dative bonding between the alkane and \( \text{cus-Pd} \) atom(s) is primarily responsible for the enhanced binding of alkanes on PdO(101).

The formation of datively-bound \( \sigma \)-complexes on PdO(101) serves to electronically activate alkane C-H bonds in addition to prolonging the surface lifetimes of these reactive precursors. This suggests the possibility that adsorbed \( \sigma \)-complexes play a general role as precursors for alkane activation on transition metal oxide surfaces. Several configurations for each alkane are identified on PdO(101), however, the local geometric features and the electronic configurations at adsorbed sites are seen to influence the initial C-H bond activation. Though dispersion constitutes a significant fraction of the alkane interaction on PdO(101) surface, dative interactions are observed to influence the specific configurations adopted by alkanes on the surface and subsequent activation pathways and barriers.

Dispersion-corrected DFT has been employed to determine initial C-H bond activation of methane, ethane and propane on PdO(101). Charge analysis demonstrate C-H bond activation of alkanes on PdO(101) to be heterolytic in nature. For methane, the subsequent bond activation of \( \text{CH}_3\text{-Pd}_{\text{cus}} \) complex has also been investigated. It is
seen that the hopping of methyl groups along $cus$-Pd row is highly facile. Furthermore, the presence of $H-O_{cus}$ is seen to influence dative bonding in the adjacent $CH_3$-$Pd_{cus}$ complexes. It is also determined that the dehydrogenation of $CH_3$-$Pd_{cus}$ as well as conversion to a $CH_3$-$O_{cus}$ species are significantly more energetically demanding than initial $CH_4$ activation, suggesting that reaction steps involving alkyl fragments determine the overall rate of alkane oxidation on PdO(101). Calculations indicate that with energy barriers for dissociation being greater than desorption barriers, methane and ethane cannot undergo facile C-H bond cleavage on PdO(101); consistent with experimental findings. However with energy barriers lesser than desorption barriers, propane complexes can undergo facile C-H bond cleavage. In addition, PdO(101) surface is observed to be highly selective towards the C-H bond cleavage of propane with a strong preference for primary bond activation. This preference is due to the greater tendency of propane molecules to populate in states where only primary C-H bonds interact strongly with the surface. Besides this, charge analysis suggest a greater substituent polarization effect that produces a more stabilizing charge distribution within the 1-propyl vs. 2-propyl TSs, which in turn causes the intrinsic energy barrier for primary C-H bond activation to be lower than that for secondary C-H bond.

Micro-kinetic models based on transition state theory have been used to simulate dissociation kinetics of methane, ethane and propane on PdO(101). The simulations demonstrate that the computed pre-factors are highly sensitive to the approach taken for calculating partition functions of the adsorbed alkane structures. Modeling all of the adsorbate motions as harmonic vibrations underestimates the entropy of the transition structure for C-H bond cleavage which results in overestimation of apparent pre-factors.
The so-called 3$N$ – 2 model, in which two frustrated adsorbate motions are modeled as free motions, predicts pre-factors that agree well with experimental estimates. For methane and ethane, the desorption pre-factors determined from the 3$N$ – 2 model are ten times smaller than the desorption pre-factors predicted by the model where all motions are treated as harmonic oscillators. For propane, besides accurately reproducing the apparent pre-factor for reaction, the micro-kinetic model estimates apparent activation energy within 14% of the experimentally determined value. While approximate, the results of the 3$N$ – 2 model represents a significant improvement in accuracy over harmonic TST and highlights the need to accurately determine the entropic contributions made by weakly-hindered motions for adsorbates on surfaces.

Dispersion-corrected DFT has also been used to investigate CO$_2$ binding and saturation on PdO(101). From the calculations, it is determined that CO$_2$ populates along the cus-Pd row till a coverage of 0.26 ML and then further populates the 4f-Pd row attaining saturation on PdO(101) at 0.52 ML. These estimates agree well with TPD results and lend confidence in the ability of the DFT-D3 method to accurately predict coverage effects. Being able to accurately predict coverage effects will assist in understanding evolution of adsorption and activation trends of various molecular species with coverage on transition metal oxide surfaces. Furthermore, these computational studies would provide valuable insight for performing site blocking experiments that could be engineered to restrict the normal reaction pathways of specific molecular species on the surface, have them partially oxidize the specie and possibly promote the generation of alternate valuable end products.
Oxidation of palladium and the chemistry of PdO(101) surface has been and is being extensively studied in our group through a combination of UHV experiments and DFT computations. The studies prove PdO(101) to be a very good catalyst for the oxidation of various molecular species. Numerous studies show that UHV experimental findings are both relevant and accurate in predicting the behavior of catalysts under normal operating conditions. Dispersion-corrected DFT calculations are seen to yield better agreement with UHV experimental estimates and provides a better description of surface events at the atomic level. Thus DFT-D3 calculations can be employed to probe molecular activity on other prospective late transition metal oxide surfaces. These computational studies will help in both guiding UHV experiments and in identifying oxide surfaces that are worthwhile to be experimentally investigated.

RuO$_2$(110) is an interesting oxide surface that has been extensively studied over the last decade. Well-defined RuO$_2$(110) layer is typically grown on Ru(0001) through dosing with O$_2$ in UHV at temperature between 550 and 700K. Through UHV experiments, Ertl et al. demonstrate methane and ethane activation on RuO$_2$(110) not facile and this observation is supported by DFT calculations. However, DFT calculations presented in Appendix B demonstrate that though the activation of lower alkanes are not facile on RuO$_2$(110), propane and higher alkanes are likely to readily activate and furthermore, the surface might selectively activate propane, similar to that observed on PdO(101) (Chapter 4).

IrO$_2$(110) surface is thermodynamically the most favored facet of Iridium (IV) oxide and is isostructural with the RuO$_2$(110) surface. However, the *cus* metal sites on these surfaces are not isoelectronic. A recent DFT study by Jiang et al. identified that
methane forms strongly-bound $\sigma$-complexes on IrO$_2$(110) and the surface is highly facile for methane activation.\textsuperscript{142} Experimental studies to grow the IrO$_2$(110) surface employ Ir(111) as an oxidation platform since the face centered cubic Ir(111) surface is analogous to the hexagonal close packing Ru(0001) surface. Though the preparation of stoichiometric oxide surface of late transition metals exhibit technical challenges, oxidation of Ir is noted to be more difficult. Over \textit{et al.} investigated oxidation of Ir(111) through a combination of DFT and \textit{in situ} surface X-ray diffraction (SXRD).\textsuperscript{143} They report the formation of rutile IrO$_2$ comprising of isolated IrO$_2$(110) and IrO$_2$(100) domains at 775 K and only at O$_2$ pressures above 100 mbar. Besides the high pressure which impedes to have the oxide structure characterized in UHV conditions, the surface is observed not to be well-ordered. Tsai \textit{et al}, were able to generate well-ordered rutile IrO$_2$(100) and corundum Ir$_2$O$_3$(001) surface through atomic oxygen exposure of Ir(111) at 550 and 600K.\textsuperscript{144} Though thermodynamic consideration prefer the rutile phase, epitaxy analysis indicates that the lattice match between Ir$_2$O$_3$(001)/Ir(111) to be superior than IrO$_2$(100)/Ir(111). Our DFT-D3 calculations determine methane activation on IrO$_2$(100) to be not as facile as IrO$_2$(110). Nevertheless, methane activation on IrO$_2$(100) is seen to be more facile than on PdO(101) and RuO$_2$(110). However, DFT-D3 calculations reveal that an oxygen rich IrO$_2$(100) surface that comprises of O atoms bound atop $\text{cus}$-Ir sites to be facile towards methane activation. Formation of these atop O atoms on IrO$_2$(100) through O$_2$ chemisorption and dissociation is seen to be favorable.
Preliminary findings on these ongoing studies of ruthenium and iridium oxide surfaces are presented in the appendices. Hopefully these results will both motivate and guide future computational and experimental studies.
APPENDIX A
METHANE ACTIVITY ON PdO(101), RuO$_2$(110), IrO$_2$(110) AND IrO$_2$(100)

A.1 Background

From computational and experimental calculations discussed in Chapter 2 to Chapter 5, it is evident that alkanes bind strongly on PdO(101) forming σ-complexes comprising of strong dative interactions with the surface. These dative interactions are seen to weaken and facilitate C-H bond cleavage and thus the σ-complexes act as precursors for bond activation. However, only propane and higher alkanes are observed to activate on PdO(101), readily decomposing to form CO$_2$ and H$_2$O. A recent DFT study highlights the IrO$_2$(110) surface to be highly facile for C-H bond activation of methane. Though IrO$_2$(110) is a relatively new oxide surface that is being investigated experimentally and computationally, this surface is seen to be isostructural with the RuO$_2$(110) surface. The growth and surface activity of RuO$_2$(110) surface towards various molecular species is well documented through rigorous experimental and computational studies over the last decade. However, compared to PdO(101), methane binds weakly on the RuO$_2$(110) surface with no observed thermal activation. Experimental studies focusing on the growth of iridium oxide surfaces report the formation of corundum Ir$_2$O$_3$(001) and rutile IrO$_2$(100)$^{143}$ or coexisting IrO$_2$(100) and IrO$_2$(110) domains.$^{144}$ In the pursuit to bring about the initial bond activation of methane, it is worthwhile to compare interaction between methane and cus metal sites on PdO(101), RuO$_2$(110), IrO$_2$(110) and IrO$_2$(100) surfaces.

A.2 PdO(101), RuO$_2$(110), IrO$_2$(110) and IrO$_2$(100) Surfaces

Bulk palladium (II) oxide crystal has a body-centered tetragonal structure where each Pd and O atom has four-fold coordination. This results in a $d$$sp^2$ hybridization type
square planar complex formation by each Pd atom and a $sp^3$ hybridization type
tetrahedral complex by O atoms. Slicing of the bulk PdO along (101) plane reveals a
surface as shown in Figure A-1. PdO(101) surface comprises of alternating rows of
 coordinatively unsaturated (cus) or three-fold and coordinatively saturated or four-fold
(4f) Pd and O atoms aligned along the [010] crystallographic direction of the bulk oxide.
The cus-Pd sites on the surface resemble a square planar complex with a coordination
vacancy directed away from one cus O and two 4f oxygen ligands.

![Figure A-1](image)

Figure A-1. Stoichiometric PdO(101) surface. Comprises of 0.35 ML of cus-Pd, cus-O,
4f-Pd and 4f-O each. $\bar{a}$ and $b$ represent the [010] and [101] crystallographic
directions of bulk PdO. The cus-Pd atoms aligned along the $\bar{a}$ direction
collectively form the cus-Pd row.

In the tetragonal rutile structure of bulk ruthenium (IV) oxide crystal, each Ru
cation is bound to six O anions while each O anion is bound to only three Ru cations.
The six and three-fold coordination by Ru and O atoms result in $sp^3d^2$ octahedral and
$sp^2$ trigonal planar complex formations, respectively. Cleavage of the bulk ruthenium
oxide crystal along the (110) plane cuts least number of Ru-O bonds and reveals a stoichiometric non-polar surface comprising of two-fold bridging (br) O, three-fold (3f) O and coordinatively unsaturated (cus) five-fold Ru atoms as shown in Figure A-2. Each of these atomic species align in separate rows along the [001] crystallographic direction of bulk ruthenium oxide. Note that both br-O and six-fold (6f) Ru atoms align on the same row with each br-O atom bound to two 6f-Ru atoms and positioned at the bridge vacancy. The cus-Ru sites resemble an octahedral complex with a coordination vacancy normal to the surface and directed away from five 3f-oxygen ligands. DFT studies indicate that the electron density about the cus-Ru and br-O atoms to be high compared to bulk atoms as each of these species expose a dangling bond.

Figure A-2. Stoichiometric RuO$_2$(110) surface. Surface exposes cus-Ru, br-O, 6f-Ir and 3f-O atoms. Note that both br-O and 6f-Ru atoms configure along the same row. $\bar{a}$ and $\bar{b}$ represent the [001] and [$\bar{1}$10] crystallographic directions of bulk RuO.
Since both bulk iridium(IV) oxide and ruthenium(IV) oxide crystals adopt tetragonal rutile structure, the (110) facets of these oxides expose metal and O atoms with similar coordination and can be compared in Figure A-2 and Figure A-3. Subtle geometric differences associated with inter-atomic distances on RuO$_2$(110) and IrO$_2$(110) surfaces are tabulated in Table A-1.

![Diagram of oxide surface]

Figure A-3. Stoichiometric IrO$_2$(110) surface. Surface exposes $cus$-Ir, $br$-O, $6f$-Ir and $3f$-O atoms. Note that both $br$-O and $6f$-Ru atoms configure along the same row. $\vec{a}$ and $\vec{b}$ represent the [001] and [110] crystallographic directions of bulk IrO.

Since RuO$_2$(110) and IrO$_2$(110) surfaces are isostructural, several DFT studies have focused specifically on comparing the chemical properties of various molecular species on these oxide surfaces. However these surfaces are not isoelectronic, especially at the $cus$ metal sites due to the difference in valence electron distribution of Ru and Ir atoms.
Table A-1. Geometric differences between isostructural RuO$_2$(110) and IrO$_2$(110) surfaces.

<table>
<thead>
<tr>
<th></th>
<th>RuO$_2$(110) (Å)</th>
<th>IrO$_2$(110) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice constants</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\bar{a}$ [direction]</td>
<td>3.13 [110]</td>
<td>3.18 [110]</td>
</tr>
<tr>
<td>$\bar{b}$ [direction]</td>
<td>6.38 [001]</td>
<td>6.42 [001]</td>
</tr>
<tr>
<td><strong>cus</strong> metal to adj.<strong>cus</strong> metal [110]</td>
<td>3.13</td>
<td>3.18</td>
</tr>
<tr>
<td>surface 3f-O to 3f-O [001]</td>
<td>2.44</td>
<td>2.44</td>
</tr>
<tr>
<td><strong>cus</strong> metal to br-O [001]</td>
<td>3.46</td>
<td>3.45</td>
</tr>
</tbody>
</table>

The (100) facet of tetragonal rutile bulk iridium oxide (shown in Figure A-4) is slightly more intricate than the IrO$_2$(110) surface. The (100) surface comprises of alternating rows of coordinatively unsaturated five-fold (**cus**) and coordinatively saturated (**6f**) Ir atoms aligning alongside two-fold bridging (**br**) and three-fold (**3f**) O atoms.

Figure A-4. Stoichiometric IrO$_2$(100) surface. Comprises of **cus**-Ir, 3f-O, 6f-Ir and br-O atoms. $\bar{a}$ and $\bar{b}$ represent the [001] and [110] crystallographic directions of bulk iridium oxide crystal. Notice that along $\bar{b}$ the surface resembles horizontally stacked tee-joints (highlighted).
Figure A-5. Partial DOS plots for *cus*-Ir atom on bare IrO$_2$(100) and IrO$_2$(110). Note that $d_{yz}$ and $d_{xz}$ states are symmetric.

The well-ordered rows align along [100] crystallographic direction of the bulk oxide. The rows of saturated and unsaturated metal cations and O anions when observed along [010] crystallographic direction resemble inclined tee-joints (highlighted) stacked on a horizontal plane forming valleys and peaks. The 6$f$-Ir atoms are embedded deep within these valleys and are not available for direct interaction with adsorbing molecular species. Similar to IrO$_2$(110), each *cus*-Ir atom on IrO$_2$(100) resembles an octahedral complex with a coordination vacancy. However on IrO$_2$(110), each *cus*-Ir atom is bound to five 3$f$-O atoms while on IrO$_2$(100) they are bound to three 3$f$-O atoms and two *br*-O atoms. Characteristics of the coordinatively unsaturated metal sites such as atomic specie, coordination number and coordination environment are recognized to influence the surface activity towards various molecular species. The dissimilar bonding
environment associated with \textit{cus}-Ir atoms on IrO$_2$(110) and IrO$_2$(100) is observed to shift the Fermi-level towards higher energy by 2.14 eV resulting in the availability of more bonding $d$ states for \textit{cus}-Ir sites of IrO$_2$(110) as illustrated in Figure A-5.

\textbf{A.3 Molecular Chemisorption of Methane on PdO(101), RuO$_2$(110), IrO$_2$(110) and IrO$_2$(100)}

\textit{n}-alkanes are seen to form $\sigma$-complexes on PdO(101) and the configuration adopted by methane on PdO(101) is well described in Chapter 5. DFT-D3 calculations predict methane to adopt an $\eta^2$ configuration on PdO(101) where H-C-H bond angle straddles a \textit{cus}-Pd atom resulting in a three-center dative interaction between two C-H bonds of the alkane and the metal atom (Figure A-7 A)). DFT-D3 predicts a zero-point corrected binding energy of 40.5 kJ/mol which agrees well with experimental estimate.\textsuperscript{40} The interactions of \textit{n}-alkanes on PdO(101) can be decomposed as dispersive and electronic, where the latter is predominantly dative interaction. These dispersion ($E_{d3}$) and electronic ($E_{dft}$) interactions can be deduced from dispersion-corrected ($E_{DFT−D3}$) energies through single point conventional DFT calculations on the DFT-D3 relaxed configurations. For \textit{n}-alkanes on PdO(101), dispersion comprises 60-64\% of the total interaction. However, force and energy analysis indicate that the dative interactions are more sensitive than dispersion and hence solely influence configuration, activation pathways and barriers of \textit{n}-alkanes on PdO(101).

Similar to PdO(101), the unsaturated metal sites on RuO$_2$(110) serve as suitable binding sites for methane. Calculations identify one stable configuration for methane on RuO$_2$(110) where the molecule straddles atop \textit{cus}-Ru adopting an $\eta^2$ configuration similar to that observed on PdO(101). However, unlike on PdO(101) where the two
surface interacting C-H bonds align along the cus-Pd row towards adjacent cus-Pd atoms, the two surface interacting C-H bonds of methane on RuO$_2$(110) align perpendicular to the cus-Ru row and towards the neighboring br-O atoms as shown in Figure A-7 B). This orientation of surface interacting C-H bonds is identified to be caused by steric hindrances from the closely arranged 3f-O atoms on the surface. DFT-D3 predicts a zero-point corrected binding energy of 37.5 kJ/mol which is in agreement with the upper bound estimate determined through Redhead analysis by Jacobi et al.$^{141}$ Dispersion effects are seen to constitute ~67% of the methane interaction on RuO$_2$(110) surface. Thus the dative interactions of methane on RuO$_2$(110) are slightly weaker compared to that on PdO(101). The weaker dative interactions on RuO$_2$(110) are seen to result in the surface interacting C-H bonds of methane experiencing almost no stretching and negligible mode softening ($<100$ cm$^{-1}$ on RuO$_2$(110) and $>200$ cm$^{-1}$ on PdO(101)) upon chemisorption.

Since both RuO$_2$(110) and IrO$_2$(110) surfaces are isostructural, configuration adopted by methane on both these surfaces are similar (compare Figure A-7 B) & C)). However these surfaces are not isoelectronic. DFT-D3 predicts enhanced binding energy of methane on IrO$_2$(110) (67.6 kJ/mol) with dispersion comprising ~50% of the interactions. Both dispersion and dative interactions of methane on IrO$_2$(110) are seen to be greater than that observed on PdO(101) and RuO$_2$(110) and is tabulated in Table A-2. Compared to RuO$_2$(110), greater dispersion interactions of methane on IrO$_2$(110) is due to the comparatively larger atomic size of the Ir metal atom.
Table A-2. Dative and dispersion interactions of methane $\eta^2$ configurations on the different metal oxide surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Electronic ($E_{dft}$) (Dative)</th>
<th>Dispersion ($E_{d3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdO(101)</td>
<td>16.1</td>
<td>24.1</td>
</tr>
<tr>
<td>RuO$_2$(110)</td>
<td>12.4</td>
<td>25.1</td>
</tr>
<tr>
<td>IrO$_2$(110)</td>
<td>33.8</td>
<td>33.8</td>
</tr>
<tr>
<td>IrO$_2$(100)</td>
<td>20.7</td>
<td>28.6</td>
</tr>
</tbody>
</table>

* Energy are reported in kJ/mol CH$_4$

Comparing density of state (DOS) plots of the $cus$ metal sites on RuO$_2$(110) and IrO$_2$(110), an offset by 0.68-0.89 eV for the different $d$ states of $cus$-Ru relative to those of $cus$-Ir towards lower energy (towards the right) is observed as indicated in Figure A-6.

![Figure A-6](image)

Figure A-6. Partial DOS plots for $cus$-Ru and $cus$-Ir atoms on bare RuO$_2$(110) and IrO$_2$(110) surfaces. Note that $d_{yz}$ and $d_{xz}$ states are symmetric and the Fermi-level on both these surfaces are equal.
However, the Fermi-level is the same for both these surfaces and this results in the availability of more $d$ states about the Fermi-level for cus-Ir atoms on IrO$_2$(110) which translates to stronger dative bonding of molecular species on this surface.

On IrO$_2$(100), methane straddles cus-Ir atom in a similar fashion as on IrO$_2$(110). The surface interacting C-H bonds align perpendicular to the cus-Ir row and are directed along the $[\bar{1}10]$ crystallographic direction as illustrated in Figure A-7 D).

![Figure A-7](image)

Figure A-7. Top and front view of η$^2$ methane configurations on the different oxide surfaces. A) PdO(101). B) RuO$_2$(110). C)IrO$_2$(110). D) IrO$_2$(100).

Though the cus metal sites on both IrO$_2$ (100) and (110) surfaces resemble an octahedral complex with a coordination vacancy directed away from the surface, the
bonding environment associated with these unsaturated metal sites are different. On \( \text{IrO}_2(110) \), each \textit{cus} metal atom is bound to five \( 3f \)-\( O \) atoms while on \( \text{IrO}_2(100) \) they are bound to three \( 3f \)-\( O \) atoms and two \textit{br}-\( O \) atoms. This difference in bonding environment is seen to result in a difference of 2.17 eV between Fermi-levels of \( \text{IrO}_2(100) \) and \( \text{IrO}_2(110) \) surfaces. The Fermi-level of \( \text{IrO}_2(100) \) being at a higher energy of -4.18 eV results in the availability of lesser \( d \) states about the Fermi-level for dative bonding as evident from the DOS plots in Figure A-5. The methane binding energies predicted by DFT-D3 for the different oxide surfaces have been tabulated in Table A-3 and can be summarized as \( \text{IrO}_2(110) > \text{IrO}_2(100) > \text{PdO}(101) > \text{RuO}_2(110) \).

**A.4 Pathways for Methane Activation on PdO(101), RuO\(_2\)(110), IrO\(_2\)(110) and IrO\(_2\)(100) Surfaces**

Illustrated in Figure A-8 are the energy diagrams for the initial C-H bond activation of methane on PdO(101), RuO\(_2\)(110), IrO\(_2\)(110) and IrO\(_2\)(100) surfaces as predicted by DFT-D3. The sum of the total energies of an isolated methane molecule and an isolated bare oxide surface is set as the reference. Accordingly, molecular states further below the reference line are more stable. The energy level of the transition state (TS) relative to the reference is termed as the apparent barrier \( \Delta E^{\pm}_{r,i} - \Delta E^{\pm}_{d,i} \). A negative apparent barrier indicates that the TS is stable enough to be sampled by the chemisorbed molecule rather than being desorbed and isolating itself from the surface.

For initial C-H bond activation of methane on PdO(101), the molecule bound atop \textit{cus}-Pd atom with its surface interacting C-H bonds directed along the \textit{cus}-Pd row rotates by \(-90^\circ\) about an axis normal to the surface. Through this rotation, the activating H atom of a surface interacting C-H bond repositions itself closer to a neighboring \textit{cus}-O atom. The C-H bond then stretches and cleaves, transferring the H-atom onto the \textit{cus}-O
atom resulting in the formation of a *cus*-OH moiety while the CH$_3$ molecule reorients itself atop *cus*-Pd atom in a rotor blade fashion with the three C-H bonds directed away from the surface.

Table A-3. Dispersion and zero-point corrected binding energies of initial, transition and final states resulting from C-H bond cleavage of methane $\eta^2$ configurations on PdO(101), RuO$_2$(110), IrO$_2$(110) and IrO$_2$(100) surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Initial state ($\Delta E_{d,i}^x$)</th>
<th>Transition State ($\Delta E_{d,i}^x - \Delta E_{r,i}^x$)</th>
<th>Final state ($E_{FS}$)</th>
<th>Reaction barrier ($\Delta E_{r,i}^x$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdO(101)</td>
<td>39.1</td>
<td>-16.1</td>
<td>75.1</td>
<td>55.2</td>
</tr>
<tr>
<td>RuO$_2$(110)</td>
<td>37.5</td>
<td>-18.6</td>
<td>55.0</td>
<td>56.2</td>
</tr>
<tr>
<td>IrO$_2$(110)</td>
<td>67.6</td>
<td>43.3</td>
<td>172.3</td>
<td>24.3</td>
</tr>
<tr>
<td>IrO$_2$(100)</td>
<td>49.3</td>
<td>-6.5</td>
<td>127.1</td>
<td>55.8</td>
</tr>
</tbody>
</table>

* Energies are reported in kJ/mol CH$_4$

On RuO$_2$(110) and IrO$_2$(110) surfaces, since the $\eta^2$ configured methane molecule binds atop *cus* metal sites with the surface interacting C-H bonds oriented towards neighboring *br*-O atoms, bond activation involves a simple stretch and cleave resulting in the formation of *br*-OH moiety and CH$_3$-metal$_{cus}$ complex. For C-H bond activation on IrO$_2$(100), the methane molecule slightly rotates (~45˚) about an axis along the coordination vacancy of the *cus*-Ir atom. The rotation brings the activating H atom close to a *br*-O atom that is across the valley. This is followed by C-H bond stretch and cleavage to form *br*-OH complex.

Though DFT-D3 predicts activation barriers within 1 kJ/mol variance for the initial C-H bond activation of methane on PdO(101), RuO$_2$(110) and IrO$_2$(100), due to the reasonable difference in the binding energies of chemisorbed methane molecules on these surfaces, the apparent barriers are widely different. Positive apparent barriers are observed for bond activation of methane on PdO(101), RuO$_2$(110) and IrO$_2$(100) while a negative apparent barrier of 43.3 kJ/mol is observed on IrO$_2$(110).
Figure A-8. Energy diagram for initial C-H bond activation of methane on PdO(101), RuO$_2$(110), IrO$_2$(110) and IrO$_2$(100). Sum of total energies of an isolated methane molecule and an isolated non-interacting bare oxide surface is taken as the reference.
The relative stability of the FSs for methane activation on the different oxide surfaces can be decomposed into stability of the CH$_3$-metal$_{cus}$ and $cus$-OH or $br$-OH complexes. It might be worthwhile to investigate the influence of the stabilities of $cus$-OH and $br$-OH complexes on the activation barriers. Beside this, DDEC charge analysis on the initial and transition states of methane on these surfaces might provide an insight into stabilization effects through charge redistribution between methane molecule and the various surface atoms during bond activation process.

**A.5 Chemisorption and Activation of Methane on Oxygenated IrO$_2$(100) surface**

On comparing chemisorption and activation of methane on IrO$_2$(110) and (100) surfaces, besides the difference in the bonding environment associated with the $cus$-Ir sites which seen to enhance methane chemisorption on IrO$_2$(110), the bonding environment associated with the $br$-O atoms onto which the activated H atom hops are also different. On IrO$_2$(110), each $br$-O atom is bound to two 6$f$-Ir atoms while on IrO$_2$(100) they are bound to two $cus$-Ir atoms. An interesting study would be to investigate if altering the bonding environment associated with the $br$-O atom involved in formation of $br$-OH complex would influence the barrier for C-H bond cleavage.

Furthermore, will this alteration have an effect on dative interactions between methane and $cus$-Ir sites. Figure A-9 illustrates three potential pathways that result from two possible case studies involving modification of the surface through oxygenation. The first scenario involves the introduction of two O atoms on top of two $cus$-Ir sites which are bound to the $br$-O atom that forms the $br$-OH complex upon initial C-H bond cleavage of methane (see IS in Figure A-9 A)). These newly introduced oxygen atoms are referred to as atop O atoms.
Figure A-9. Chemisorption and initial C-H bond activation pathways for methane on oxygenated IrO$_2$(100) surface. A) Activation pathway for methane resulting in the formation of br-OH complex, where both the cus-Ir atoms that are bound to the br-O atom forming the complex, hosts atop O atoms. B) Activation pathway for methane on an oxygenated IrO$_2$(100) surface resulting in the formation of br-OH complex. The cus-Ir atom that neighbors the chemisorbed methane molecule hosts an atop O atom. C) Activation pathway for methane forming atop-OH complex on an oxygenated IrO$_2$(100) surface, where the cus-Ir atom that neighbors the chemisorbed methane molecule hosts an atop O atom. Note that the atop O atoms have been highlighted.
The second possibility involves introducing an atop O atom onto the *cus*-Ir atom that neighbors the bound methane molecule (see IS in Figure A-9 B) or C). This second setup is seen to result in two possible pathways for C-H bond cleavage, i) hopping of activating H atom onto the *br*-O atom to form *br*-OH complex as shown in Figure A-9 B) and ii) hopping of H atom onto the atop O atom to form atop-OH complex as shown in Figure A-9 C).

Introduction of these atop O atoms are seen to both enhance methane binding on the surface and is accompanied with notable reduction in activation barriers. When an atop O atom is placed on a neighboring *cus*-Ir site, significant strengthening of methane interaction with the surface is observed (64.7 kJ/mol). Comparing Figure A-9 B) and Figure A-9 C), an interesting observation made is that the barriers are lesser influenced by the strength of interaction between methane molecule and *cus*-Ir site and seemingly more influenced by the bonding environment associated with the O atom that forms the OH complex.

For situations illustrated in Figure A-9 B) and C), based on geometric reconfigurations (rotation) associated with the methane molecule during the activation process, one would expect a lower barrier for the H transfer on the *br*-O atom since it involves the least rotation. However, the barrier for formation of atop-OH complex is favored over *br*-OH complex by 25.4 kJ/mol. Furthermore, studies of methane activation on PdO(101) indicate that the potential energy surface associated with rotation of methane on top of *cus*-Pd atom to be rather flat. Detailed DDEC charge analysis and charge density plots might provide an explanation for these observations.
A.6 Oxygen Chemisorption and Dissociation on IrO$_2$(100)

The C-H bond activation pathways described in the previous section are worthwhile to be investigated from an experimental stand point only if it possible to form the so-called atop O atoms. Hence the chemisorption and dissociation of O$_2$ on IrO$_2$(100) surface were also investigated. DFT-D3 calculations predict strong binding of oxygen molecule at the bridge site between adjacent cus-Ir atoms on IrO$_2$(100). Through NEB calculations, it is determined that the oxygen molecule bound at the bridge sites can readily dissociate, resulting in the formation of atop O atoms on the neighboring cus-Ir sites as illustrated in Figure A-10.

![Figure A-10. O$_2$ chemisorption and dissociation on IrO$_2$(100).](image)

A recent study by Over et al. report that the gaseous exposure of hydrochloric acid on RuO$_2$(110) results in the replacement of the br-O atoms with Cl anions and forms H$_2$O as a byproduct.$^{146}$ These br-Cl atoms would deactivate the neighboring cus-metal site. Thus through chlorination of IrO$_2$(110) or IrO$_2$(100) surfaces, partial oxidation
of alkanes may be achieved and this might promote the formation of higher valuable organic molecules.
APPENDIX B
PROPAINE SELECTIVITY ON RuO$_2$(110) AND IrO$_2$(110)

B.1 Background

Chemisorption, activation and selectivity of propane on PdO(101) is well described in Chapter 4. Studies report methane and ethane bind weakly on RuO$_2$(110) with no noticeable thermal activation. However, the activity of propane on this oxide has not been investigated. Based on the similarity of methane binding configurations on RuO$_2$(110) and PdO(101), propane and higher alkanes are likely to adopt a similar bonding configuration on RuO$_2$(110) as observed on the PdO(101) surface, where it comprises of multiple $\eta^1$ dative interactions along cus metal row. Multiple $\eta^1$ interactions of propane on RuO$_2$(110) are likely to increase desorption energies and thus yield negative apparent barriers which would suggest propane activation on RuO$_2$(110) to be facile. Furthermore, based on enhancement of methane dative interactions on the IrO$_2$(110) surface relative to PdO(101) and RuO$_2$(110) oxide surfaces, propane activation on this surface is likely to be highly facile. An interesting addition to this study would be to investigate whether propane activation on RuO$_2$(110) and IrO$_2$(110) exhibits similar preference for primary C-H bond activation as observed on PdO(101).

B.2 Pathways for Propane Activation on RuO$_2$(110) and IrO$_2$(110)

Illustrated in Figure B-1 are the energy diagrams for the initial bond activation of primary and secondary C-H bonds of staggered propane configurations on RuO$_2$(110) and IrO$_2$(110). The negative apparent barriers indicate propane activation to be facile on both these surfaces and based on the energies of initial and transition states, a strong preference for the primary C-H bond activation of propane on these surfaces is observed.
Figure B-1. Energy diagram for initial bond activation of primary and secondary C-H bonds in staggered propane configurations on RuO$_2$(110) and IrO$_2$(110). Sum of total energies of an isolated propane molecule and an isolated non-interacting bare oxide surface is taken as the reference.
Greater fractional population of primary bound configurations due to the higher desorption energies resulting from two dative interactions and better charge distribution within 1-propyl groups due to a dative interaction that remains intact throughout the activation process are likely reasons for the observed preference of primary C-H bond activation propane on these oxide surfaces. DDEC analysis would give a better picture of charge stabilization effects during the activation process. Furthermore, since the growth of RuO$_2$(110) surface is already well established, experimental studies of propane on RuO$_2$(110) might help in further investigating the so-called 3$\text{N}–2$ model.

Preliminary calculations of propane activation on IrO$_2$(100) indicate a similar preference for primary C-H bond activation. However, the calculations indicate positive apparent barriers for both primary and secondary bound configurations suggesting the pathways are not facile.


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<th>Year</th>
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BIOGRAPHICAL SKETCH

Abbin Antony was born in November 1985 in Hofuf, Saudi Arabia to Antony V. Devasia and Lify Antony. He was raised in Riyadh, Saudi Arabia, where he attended the International Indian School (I.I.S.R) which is affiliated to the Indian Central Board of Secondary Education (C.B.S.E). Upon his graduation as a science major in 2002, he enrolled for an undergraduate degree in chemical engineering at Thangal Kunju Musaliar College of Engineering (T.K.M.C.E.) which is affiliated to the University of Kerala in India. During his undergraduate studies, he both worked as a trainee at Hindustan Organic Chemicals Ltd. and as an intern at Kochi Refineries-Bharat Petroleum Corp Ltd. For his internship at the refinery, he worked on optimizing the polyisobutene production unit (PIBU). In the August of 2007, Abbin attained his Bachelor of Technology (B.Tech) degree in chemical engineering with distinction. He then enrolled for his master’s degree in chemical engineering at University of Florida in the fall of 2008. During his master’s program, under the guidance of Dr. Spyros A. Svoronos and Dr. Hassan El-Shall, he worked on a project to translate a batch technique for the separation of dolomite from phosphate into a continuous process for the fertilizer company Mosaic. In the December of 2010, Abbin attained a Master of Science (M.S.) degree in chemical engineering from University of Florida and was also offered an opportunity to pursue his doctoral degree. Under the supervision of Dr. Jason F. Weaver and Dr. Aravind R. Asthagiri, Abbin performed \textit{ab initio} quantum mechanical studies to explore different late-transition metal oxide surfaces and investigate chemical activity of various molecular species on these surfaces. In the August of 2013, Abbin earned his Doctor of Philosophy (PhD) degree in chemical engineering and moved to
Hillsboro, Oregon to join the multinational semiconductor chip maker Intel as a process engineer.