First Principles Insights into the Mechanism of Pyridine-Catalyzed CO₂ Reduction on p-GaP Photoelectrodes

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A DISSERTATION PRESENTED TO THE FACULTY OF PRINCETON UNIVERSITY IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE BY THE DEPARTMENT OF CHEMISTRY

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September 2017
Abstract

Photoelectrochemical CO₂ reduction is a promising technology for the sustainable production of liquid fuels but presents some fundamental challenges. Overcoming these challenges requires the development of efficient catalysts, which could be accelerated by the discovery of the chemical mechanism by which existing successful catalysts operate. This dissertation uses quantum-mechanics-based simulations to investigate the CO₂ reduction mechanism in a photoelectrochemical system that uses a p-GaP photoelectrode and a pyridine (Py)-based co-catalyst in an acidified aqueous solution. In particular, we develop accurate models of the electrode solution/interface and use density functional theory methods to compute relevant properties of species at this interface. Based on these properties, we gain mechanistic insights, assess the validity of previously proposed mechanisms, and hypothesize and test new mechanisms.

A long-standing mechanistic hypothesis is that the homogeneous reduction of pyridinium (PyH⁺) to the 1-pyridinyl radical (1-PyH•) is an essential step for formation of the active catalyst. Herein we show that 1-PyH• is unstable and spontaneously transfers its electron to the electrode surface. In addition, we find at most a very small thermodynamic driving force for this reduction step; PyH⁺ is reduced instead more favorably to intermediates contributing to possible formation of adsorbed dihydropyridine (DHP), a co-catalyst proposed in an alternative mechanism. Moreover, we provide strong evidence based on our calculations and experimental observations that the mechanism cannot be fully homogeneous and must involve surface-bound intermediates.

Adsorbed DHP was proposed to form via surface hydride and aqueous proton transfer to adsorbed Py and to subsequently reduce CO₂ by transferring hydride to it. In a combined
experimental-theoretical characterization of the electrode/solution interface, we find that water
dissociation is thermodynamically favorable at this interface, producing stable adsorbed protons
that could reduce to surface hydrides under operating conditions. In another combined
investigation, we find that adsorbed Py reactivity supports the proposed mechanism for adsorbed
DHP formation. Additionally, our calculations show that the proposed hydride transfers, unlike
adsorbed proton transfers, are thermodynamically favored. However, we find that adsorbed DHP
formation is likely kinetically hindered. We therefore propose and investigate alternative co-
catalytic intermediates that might form and react with CO₂ more favorably.
Acknowledgements

Many people have helped and supported me over the past five years as I worked towards the completion of my graduate work at Princeton. I would like to acknowledge them in the following, along with the people who inspired me and made it possible for me to come to Princeton in the first place.

First and foremost, I would like to thank my advisor, Dean Emily Carter, without whom this thesis work would not have been possible. In my first year at Princeton, you welcomed me in your research group where I found myself surrounded by people eager to help me get started on a new and exciting research adventure. In the past five years, you have been so supportive and always available to help in spite of your many responsibilities. You have also been and will always be a great role model for me. Seeing what you have accomplished as a woman in science has made me stronger and more confident, and I am so indebted to you for that. You have taught me to think critically and independently. You have pushed me to have high standards in my research practice, and you have taught me how to meet my goals. I am also grateful for the resources you invested in my education and professional development. During my graduate career, I have had the opportunity to attend conferences in beautiful places and discuss my work with many interesting people. You have allowed me to have numerous teaching and mentoring experiences because you understood my passion for these activities and you trusted that they would not interfere with my research progress. It is needless to say that your constant support and mentorship have been invaluable for my success in graduate school and for my future career.

I also would like to acknowledge the other members of my thesis advisory committee. I would like to thank Professor Bruce Koel for serving as second reader of my dissertation and for
collaborating with me on some of the projects that are part of this dissertation. I have had very
useful discussions with Professor Andrew Bocarsly and his research group regarding their
experiments and electrochemistry in general. Professor Annabella Selloni offered very helpful
advice when I first started my Ph.D. and has given me useful feedback on my work over the
years. Finally, I would like to thank Professor Abigail Doyle for serving on my out of field
proposal committee.

Many current and previous members of the Carter research group have played an
important role in my academic experience at Princeton, and I want to thank them for this. Dr.
Christoph Riplinger was my mentor when I first started working on my research project, and I
could not have asked for a better person to be in that role. He was always ready to help and
advise me, whether I was having troubles with my research or needed help buying a car. I would
also like to thank the many people who welcomed me and helped me get started in the group:
Professor John Keith, Professor Ana Muñoz-García, Professor Michele Pavone, Dr. Johannes
Dieterich, Dr. Nima Alidoust, Dr. Andrew Ritzmann, Dr. David Krisiloff, Dr. Dalal Kanan, and
Dr. Leah Isseroff Bendavid. I am especially grateful to Dr. Johannes Dieterich and Ms. Nari
Baughman for their invaluable help with the writing of this dissertation. I would also like to
thank Dr. Thomas Senfile for collaborating with me in the past two years. Special thanks go to
various group members for innumerable helpful discussions: Dr. Nima Alidoust, Dr. Johannes
Dieterich, Dr. Andrew Ritzmann, Dr. Christoph Riplinger, Dr. Kuang Yu, Dr. Thomas Senfile,
Dr. Mark Martirez, Alexander Tkalych, Dr. Houlong Zhuang, and Chuck Witt. Thank you for all
of the questions you have answered and for all the questions you have asked; you have helped
me become a better scientist.
In addition, I would like to thank my collaborators outside of the Carter group: Professor Coleman Kronawitter and Melissa Clark. Working with you both was a pleasure and a great educational experience. I feel very lucky and hope to have more collaborators like you in the future.

I would like to acknowledge the Air Force Office of Scientific Research for funding my research and for computational resources, the Computational Science and Engineering Support group and TIGRESS computer cluster at Princeton for computational resources, Princeton University, and the Department of Chemistry. In particular, I would like to thank my department graduate administrators Ms. Meghan Krause and Ms. Meredith La Salle-Tarantin for all of their help and encouragement as I reached each milestone of the Ph.D. program in Chemistry. Dr. Robert L’Esperance has also been very helpful and supportive during my teaching experience in the Department of Chemistry and during the job search process.

I have had the pleasure to be part of various centers and institutes during my time at Princeton: the Writing Center, the McGraw Center for Teaching and Learning, and the Freshman Scholars Institute. My teaching and mentoring experiences have been a great complement to my research experience, and they were crucial for helping me decide what career direction to take. I would also like to thank Dr. Susanne Killian at the Office of Career Services for all of her help and support during the job search process. I am also grateful to all of my students for making my time at Princeton more fun and meaningful!

Many thanks go to the people who have been close to me during my time at Princeton. First and foremost, I would like to thank Ben for being constantly there for me over the past five years. We discovered that graduate school can have some challenges, but we learned how to
overcome them together and make each other stronger. Christoph, Barbara, Nima, and Solmaz have been wonderful friends, and I hope we will manage to stay close in the upcoming years. I would also like to thank Hsin-Yu for all his invaluable help in my first year at Princeton, and Jake for all of the fun we have had while writing our dissertations together. I want to thank Mary for all of the relaxing lunch breaks. Finally, I am thankful to Luca for welcoming me to the United States when I first arrived and for a great friendship over the past five years.

I would also like to thank all of the people who inspired me to pursue a Ph.D. in the first place. My high school chemistry teacher Alessandra Melloni and my undergraduate advisor Dr. Anna Maria Ferrari helped me discover my passion for chemistry and research. I am especially grateful to Dr. Anna Maria Ferrari for pushing me to pursue a research experience abroad and to the other faculty members of the Department of Chemistry at the University of Torino for helping me make that possible. I would also like to thank Professor Francesco Paesani at the University of California, San Diego for his advice during the graduate school application process and over the past five years.

Finally, a big thank you goes to my family and friends back home in Italy. They understood how important this experience would be for me and pushed me to pursue it. I will be forever grateful to my mother, who supported me throughout my life, made so many sacrifices to give me the best opportunities she could, advised me when I needed it, and trusted me without a doubt when I had to make my own decisions. I would also like to thank my mother’s partner Marco for supporting me and being proud of me as if I were his own daughter. I would like to thank my father for all of the effort he has put into strengthening our relationship and supporting me over the past five years. I want to thank my brother, Filippo. I am sorry I left when you were
still so little but am grateful for the very special and fun time we had together when you came to visit me. I am so proud of you, and I can’t wait to see what you will do next. Finally, I am so grateful to my amazing friends Giulia, Vanja, and Riccardo for always being there for me in spite of the long distance.
List of Prior Publications and Presentations

Materials from this dissertation have been previously published or accepted for publication:


Materials from this dissertation have been previously presented publicly at scholarly conferences or meetings:

- “Pyridine-Catalyzed CO₂ Reduction on p-GaP Electrodes: First-principles Investigation of Possible Reaction Mechanisms”, talk at the 249th ACS Spring National Meeting, March 26, 2015, Denver, CO
- “First-Principles Investigation of the Role of Pyridinium and Adsorbed Dihydropyridine in Pyridine-Catalyzed CO₂ Reduction on p-GaP Photoelectrodes”, talk at the 251th ACS Spring National Meeting, March 13, 2016, San Diego, CA
- “Pyridine-Catalyzed Photocatalytic Reduction of CO₂ on GaP Electrodes”, poster at the 2nd Annual Meeting of the Princeton E-ffiliates Partnership, November 15, 2013, Princeton, NJ
- “Towards Understanding Pyridine-Catalyzed Photocatalytic Reduction of CO₂ on GaP Electrodes”, poster at the AFOSR MURI Annual Review Meeting, December 9, 2013, La Jolla, CA
- “New Insights into the Mechanism of Pyridine-Catalyzed CO₂ Reduction on GaP Electrodes”, poster at the American Conference on Theoretical Chemistry (ACTC), July 22, 2014, Telluride, CO
• “New Insights into the Mechanism of Pyridine-Catalyzed CO₂ Reduction on GaP Electrodes”, poster at the 3rd Annual Meeting of the Princeton E-ffiliates Partnership, November 14, 2014, Princeton, NJ

• “Pyridine-Catalyzed CO₂ Reduction on GaP Electrodes: Can Surface Hydrogen Atoms Play a Role?”, poster at the AFOSR MURI Annual Review Meeting, January 20, 2015, San Diego, CA

• “Pyridine-Catalyzed CO₂ Reduction on GaP Electrodes: Can Surface Hydrogen Atoms Play a Role?”, poster at the Third Biennial CO₂ Workshop, March 16, 2015, Princeton, NJ


• “Pyridine-Catalyzed CO₂ Reduction on p-GaP Electrodes: New Insights on the Role of Pyridinium from Theoretical Investigations”, poster at the AFOSR MURI Annual Review Meeting, January 25, 2016, San Diego, CA

• “Pyridine-Catalyzed CO₂ Reduction on p-GaP Electrodes: New Mechanistic Insights from First-Principles Investigations”, poster at the Andlinger Center Building Opening Celebration and Symposium, May 19, 2016, Princeton, NJ
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Chapter 1

Introduction*

Numerous studies predict that the world total energy consumption will continue increasing due to population growth and developing economies, with projections ranging from a 30% to 50% increase within the next 20 years.\textsuperscript{1,2} Anthropogenic carbon dioxide emissions due to fossil fuel burning are very likely to be one of the dominant causes of global warming, according to the most recent assessment report by the Intergovernmental Panel on Climate Change.\textsuperscript{3} In this scenario, it is imperative that we displace fossil fuels and identify renewable and carbon-neutral energy sources to ensure our economic stability and preserve our environment. Electric power can be generated with a portfolio of sustainable and carbon-neutral solutions available today, such as wind and solar, which are projected to become cost-competitive with fossil fuels in the near future.\textsuperscript{4} However, liquid fuels will still be necessary for heavy-duty transportation, and we therefore must identify a more sustainable way to produce them. This dissertation focuses on one such promising avenue for the sustainable production of liquid fuels that can also contribute to the mitigation of anthropogenic carbon dioxide emissions: photoelectrochemical carbon dioxide reduction.

1.1 Photoelectrochemical Carbon Dioxide Reduction to Liquid Fuels

Photoelectrochemical carbon dioxide reduction is a process in which carbon dioxide is converted into a useful product (e.g., liquid fuels or other reactant molecules needed for the synthesis of

liquid fuels) by using the energy of artificial or solar light. Solar energy is extremely abundant, with technologies to harvest this type of energy becoming increasingly cost-effective. However, solar energy must be converted into a different form of energy in order to be stored, transported where needed, and made available when needed. Solar-powered carbon dioxide conversion into liquid fuels provides us with a strategy for solar energy storage into chemical form, i.e., the so-called “solar fuels.” Solar water splitting represents an alternative solution for storing solar energy by producing a fuel, in this case, H₂. However, H₂ presents two major drawbacks as an energy vector: 1) it has a low energy density for practical large-scale use, and 2) it is not well suited for our current transportation infrastructure. Hydrocarbon-based solar fuels do not present these limitations and thus are preferable to H₂. On the other hand, H₂ is a main component of syngas, which can be converted into fuels via the Fischer-Tropsch process. Another advantage of hydrocarbon-based solar fuels is that they would also contribute to the mitigation of anthropogenic CO₂ emissions, given that CO₂ is the feedstock for the fuel production. However, CO₂ utilization will only delay our impact on the Earth’s climate, so carbon capture and sequestration technologies ultimately must be employed to effectively reduce CO₂ atmospheric concentration.

There are some fundamental challenges associated with the reduction of CO₂. These challenges need to be overcome in order to make hydrocarbon-based solar fuel production more efficient. First, CO₂ is characterized by high thermodynamic stability as demonstrated by the large formal electrochemical reduction potential (E°') for the one-electron reduction of CO₂ (-1.85 vs. standard hydrogen electrode (SHE) at pH=7). Lower E° values are found when CO₂ is reduced via proton-coupled multi-electron transfer steps because more stable products are generated (e.g., HCOO⁻, CO, H₂CO, CH₃OH, and CH₄, see Table 1.1). However, high activation
energies are typically associated with such proton-coupled multi-electron transfer steps and are reflected in the slow kinetics of the reduction process. Under these conditions, overpotentials (i.e., potentials more negative than the thermodynamic reduction potential) must be applied to drive the reaction at a reasonable rate. Another fundamental challenge is represented by the fact that reduction of protons, which are needed for the reduction of CO$_2$ to more thermodynamically stable products, occurs at a similar potential to CO$_2$ reduction (Table 1.1). Consequently, the hydrogen evolution reaction (HER) and other competing reactions can severely limit the efficiency of the CO$_2$ reduction process.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^{0*}$ vs. SHE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + e$^-$ → CO$_2^{-}$</td>
<td>-1.85</td>
</tr>
<tr>
<td>CO$_2$(g) + H$_2$O(l) + 2e$^-$ → HCOO$^-$(aq) + OH$^-$ (aq)</td>
<td>-0.665</td>
</tr>
<tr>
<td>CO$_2$(g) + H$_2$O(l) + 2e$^-$ → CO(g) + 2OH$^-$ (aq)</td>
<td>-0.521</td>
</tr>
<tr>
<td>CO$_2$(g) + 3H$_2$O(l) + 4e$^-$ → H$_2$CO(aq) + 4OH$^-$ (aq)</td>
<td>-0.485</td>
</tr>
<tr>
<td>CO$_2$(g) + 5H$_2$O(l) + 6e$^-$ → CH$_3$OH(aq) + 6OH$^-$ (aq)</td>
<td>-0.399</td>
</tr>
<tr>
<td>CO$_2$(g) + 6H$_2$O(l) + 8e$^-$ → CH$_4$(g) + 8OH$^-$ (aq)</td>
<td>-0.246</td>
</tr>
<tr>
<td>2H$_2$O(l) + 2e$^-$ → H$_2$(g) + 2OH$^-$ (aq)</td>
<td>-0.414</td>
</tr>
</tbody>
</table>

Table 1.1 Formal electrochemical reduction potential ($E^{0*}$) relative to the standard hydrogen electrode (SHE) at pH=7 for reactions relevant to catalytic CO$_2$ reduction. Data taken from Ref. 8.

The fundamental challenges associated with CO$_2$ reduction can be partly overcome by employing an electrocatalyst or a photoelectrocatalyst that can selectively facilitate the electron transfer and chemical steps for CO$_2$ reduction.$^7$ Photoelectrocatalysts present a greater advantage
in that they can directly harness the electrons needed for the CO₂ reduction process from sunlight. The figures of merit for CO₂ reduction (photo)electrocatalysts typically employed in the literature are the overpotential, which has already been introduced, and the Faradic efficiency, which is a measure of the selectivity of the catalyst. The Faradaic efficiency is given by the ratio between the actual amount of desired CO₂-reduction products obtained and the theoretical amount expected based on the number of electrons passed. The best (photo)electrocatalyst will have the lowest overpotentials and the highest Faradaic efficiency.

Many (photo)electrocatalysts for CO₂ reduction have been developed and tested in recent decades with varying degrees of success. An overview of these systems is beyond the scope of this thesis; however, excellent review articles on both electrocatalysts and photoelectrocatalysts are available for the interested reader. Here, we will instead focus on introducing the reader to the photoelectrocatalytic system under investigation in this dissertation. In this system, which was developed by Professor Andrew B. Bocarsly’s research group at Princeton University, CO₂ is selectively reduced to methanol by using a p-GaP photocathode in contact with an acidified aqueous solution containing pyridine (Py). More details on this system are provided in section 1.3, where we discuss various experimental and computational studies related to this system as well as provide an overview of the debate on the mechanism. The goal of this dissertation is to provide useful mechanistic insights on the catalytic CO₂ reduction process occurring in this system for the scientific community working on CO₂ reduction in order to develop improved photoelectrocatalysts.
1.2 Role of Quantum-Mechanics-Based Simulations

Computational chemistry and more specifically quantum-mechanics-based simulations can play a major role in the development or improvement of (photo)electrocatalytic systems for CO₂ reduction. In general, these types of simulations allow us to calculate properties of molecules and materials at the atomic scale, which can be too difficult to be measured by experiments. Quantum-mechanics-based methods are particularly suited for the study of photoelectrocatalytic applications because they allow us to predict the behavior of electrons. Furthermore, these methods have the great advantage of not requiring experimental input. The application of quantum-mechanics-based methods therefore is not limited to well-characterized experimental systems, and such methods can be used to predict properties of novel molecules and materials.

Provided that a quantum method capable of correctly capturing the physics of the system under study has been chosen, quantum-mechanics-based simulations allow us to calculate electronic energy levels and electron spatial distributions from which various properties of molecules and materials can be derived. Quantum mechanics therefore is a powerful tool that can complement experiments in the search for efficient and inexpensive (photo)electrocatalysts for reducing CO₂ to liquid fuels, as demonstrated by this thesis work. For instance, as we will show in Chapter 6, quantum-mechanics-based simulations can be used to calculate the electrode material band edge positions under relevant operating conditions (e.g., exposure to aqueous solution) and to predict the reduction potentials of postulated reactions. Based on these properties, which can be difficult to measure via experimental techniques, one can determine which reactions can occur by transfer of photoexcited electrons from a semiconductor photocathode.
Once the properties of interest have been calculated, they can be used together with relevant experimental observations to propose a catalytic mechanism for the system under study. This mechanism then can be validated by designing appropriate experiments. Knowledge of the mechanism at work in existing catalytic systems can help us optimize reaction conditions and synthesize better catalysts to maximize the yield of the desired CO₂-reduction product, ultimately making photoelectrochemical CO₂ reduction a competitive technology for liquid fuel production. The ultimate goal of this dissertation is to contribute to the design of improved photoelectrocatalytic systems for CO₂ reduction by providing significant insights into the catalytic mechanism at work in the system developed by Bocarsly and co-workers.¹¹

1.3 Pyridine-Catalyzed CO₂ Reduction

Bocarsly and co-workers have reported Py-catalyzed CO₂ reduction on various electrode materials over the past three decades.¹¹,¹⁴–¹⁶ In this thesis work, we focus on unravelling the catalytic mechanism of Py-catalyzed CO₂ reduction on p-GaP photocathodes. This system is characterized by the highest Faradaic efficiency and overpotential reduction (vide infra), making it superior according to the figures of merit for CO₂ reduction photoelectrocatalysts introduced above. Given the promising features of this system, understanding the mechanism of Py-catalyzed CO₂ reduction would constitute a fundamental advance towards the design of efficient photoelectrocatalytic systems for the conversion of CO₂ into fuels. Since the Bocarsly report on p-GaP photocathodes, many experimental and computational groups have conducted further studies on Py-catalyzed CO₂ reduction. Here, we present a brief overview of these studies, focusing on the results that provide motivation for the research performed and presented in this dissertation.
1.3.1 Relevant Experimental Reports of Pyridine-Catalyzed CO₂ Reduction

Bocarsly and co-workers first reported Py-catalyzed CO₂ reduction on Pd electrodes in 1994.¹⁴ The selectivity of the process was not particularly high (30% Faradaic efficiency), but their system operated at very low overpotentials. In this study, the pH of the aqueous solution containing Py was set equal to 5.4, and no reduction phenomena associated with Py were observed for pH values above 7. Based on these observations, the authors concluded that the protonated form of Py, pyridinium (PyH⁺, \( pK_a = 5.3 \)), was needed in order for catalytic CO₂ reduction to occur.

In 2008, Bocarsly and co-workers reported Py-catalyzed CO₂ reduction with significantly improved performance on p-GaP photocathodes under illumination.¹¹ Also in this study, the pH of the aqueous solution was set almost equal to the PyH⁺ \( pK_a \). With this experimental setup, Bocarsly and co-workers observed CO₂ reduction to methanol with Faradaic efficiency near 100%, at underpotentials greater than 300 mV \( (i.e., \) they applied a potential that was 300 mV less negative than the thermodynamic potential for CO₂ reduction to methanol).¹¹ Previous experimental work showed that good Faradaic efficiency can also be obtained in the absence of Py when using a p-GaP photocathode.¹⁷,¹⁸ However, these experiments required large overpotentials to obtain CO₂ reduction products. The different outcome of the experiments performed by Bocarsly and co-workers in terms of overpotential and Faradaic efficiency suggests that Py or a species derived from it plays a crucial catalytic role in the reduction of CO₂.

Since the 2008 report by Bocarsly and co-workers, Py-catalyzed CO₂ reduction to various products has been reported on other semiconductor photocathodes and metal electrodes,
with varying outcomes in terms of Faradaic efficiency and applied potential. Some of the most promising results were obtained on CuInS$_2$\textsuperscript{19,20} and CdTe\textsuperscript{21} photocathodes. Yuan and Hao reported CO$_2$ reduction to methanol at 97\% Faradaic efficiency and 20 mV overpotentials over CuInS$_2$ electrodes\textsuperscript{19} while Jeon and co-workers observed a 20\% Faradaic efficiency increase for the reduction of CO$_2$ to formic acid when adding Py to the aqueous solution in contact with a CdTe electrode\textsuperscript{21}.

Overall, these experimental observations provide preliminary insight into the catalytic mechanism. First, CO$_2$ reduction over p-GaP photocathodes at underpotentials was observed only when Py was added to the aqueous solution in contact with the electrode, suggesting that Py or a species derived from it is necessary for the catalysis. Second, the pH dependence of the experimental outcomes suggests that PyH$^+$ or more generally an acidic pH is necessary for catalytic CO$_2$ reduction to occur. Finally, the different degrees of selectivity and magnitude of overpotentials observed when using different electrodes suggest that the electrode surface might also be participating in the catalytic mechanism.

1.3.2 Proposed Mechanisms and Debate on the Mechanism

Bocarsly and co-workers initially suggested a homogeneous mechanism involving PyH$^+$, based on the observed pH dependence of the experimental outcomes\textsuperscript{14,15}. In this mechanism, PyH$^+$ is first reduced to the 1-pyridinyl radical (1-PyH$^+$), which then forms a carbamate complex with CO$_2$, driving its reduction (Figure 1.1).
Figure 1.1 Initial steps of the mechanism for pyridine (Py)-catalyzed CO$_2$ reduction proposed by Bocarsly and co-workers.$^{14,15}$ Pyridinium (PyH$^+$) is reduced to the 1-pyridinyl radical (1-PyH$^-$). 1-PyH$^-$ then forms a carbamate complex with CO$_2$ and ultimately leads to its reduction to methanol.

The mechanism proposed by Bocarsly and co-workers was disproved by subsequent computational studies. First, multiple groups independently found that the computed reduction potential for the homogeneous reduction of PyH$^+$ to 1-PyH$^-$ (-1.44 V,$^{22}$ -1.44 V,$^{23}$ -1.31 V,$^{24}$ and -1.58 V$^{25}$ vs. the saturated calomel electrode (SCE)) is significantly more negative than the potential applied in the experiments conducted on Pt electrodes by Bocarsly and co-workers (-0.58 V vs. SCE on Pt).$^{15}$ Keith and Carter validated the accuracy of their computed reduction potentials for a series of substituted PyH$^+$ species by comparing to experimental values and found agreement to within 0.2 V.$^{23}$ Based on the fact that the error in their computed reduction potentials (0.2 V) is significantly smaller than the deviation between their computed reduction potential for unsubstituted PyH$^+$ (-1.44 V) and the potential applied by Bocarsly and co-workers (-0.58 V vs. SCE), they concluded that their computational method is accurate enough to rule out the hypothesis of homogeneous PyH$^+$ reduction to 1-PyH$^-$ at Pt electrodes. However, this result only excludes the possibility of 1-PyH$^-$ formation at metal electrodes. Further investigations are needed in order to exclude the possibility of 1-PyH$^-$ formation at semiconductor electrodes (vide
First, the pK$_a$ of 1-PyH$^+$ was found to be ~27 in two independent theoretical studies.$^{23,24}$ Based on this result, Keith and Carter argued that the proposed carbamate species is unlikely to form because its formation likely requires an unfavorable deprotonation of 1-PyH$^+$.\textsuperscript{23}

In response to this conclusion, Musgrave and co-workers suggested that the pK$_a$ is not a relevant quantity for establishing the viability of this reaction, since they predicted that the electron transfer from 1-PyH$^+$ to CO$_2$ occurs prior to the proton transfer.\textsuperscript{24} As a consequence, the pK$_a$ of the partially oxidized 1-PyH$^+$ gets lowered, and the reduction becomes more feasible. To further support this finding, they showed that the activation energy for the proton/CO$_2$ exchange reaction is low enough for this process to be feasible under experimental conditions as long as several explicit water molecules mediate the proton transfer. In contrast, Keith and Carter found a barrier consistently greater than 30 kcal/mol for the same process even in the presence of explicit water molecules.\textsuperscript{26} They explained this discrepancy with the neglect of entropic contributions in the simulations of Musgrave and co-workers.\textsuperscript{26} Overall, these findings provide strong evidence for ruling out the mechanism for Py-catalyzed CO$_2$ reduction proposed by Bocarsly and co-workers. In addition, this mechanism is homogeneous and as such cannot explain the observed electrode dependence of selectivity and applied potential in the experiments discussed in the previous section.

After the disproval of the mechanism proposed by Bocarsly and co-workers, two alternative mechanisms, both heterogeneous, were proposed in 2013 by two computational research groups. Batista and co-workers proposed an alternative heterogeneous mechanism for the reduction of CO$_2$ on Pt electrodes catalyzed by PyH$^+$ (Figure 1.2).\textsuperscript{25} In this mechanism, the electrode surface is directly involved in the catalytic process. In the first step, PyH$^+$ is reduced to Py in solution and an adsorbed hydrogen atom on the Pt surface; for this step they calculated a
reduction potential (-0.72 V vs. SCE) that is in good agreement with the measured one (-0.58 V vs. SCE). In the second step, CO₂ is reduced to formic acid by a surface hydride and a proton coming from PyH⁺.

Figure 1.2 Mechanism proposed by Batista and co-workers for heterogeneous pyridine (Py)-catalyzed CO₂ reduction on Pt electrodes. In the first step pyridinium (PyH⁺) undergoes a one-electron reduction to an adsorbed hydrogen atom and Py in solution. In the second step, the adsorbed hydrogen atom and a second electron are transferred to CO₂ along with a proton coming from a second PyH⁺ molecule, resulting in the formation of HCOOH.

Although the mechanism proposed by Batista and co-workers is consistent with the measured applied potential on Pt and has low predicted activation barriers, it does not explain why PyH⁺ is specifically required for the catalysis to occur. In fact, the only role for PyH⁺ in this mechanism is to act as a proton donor, which could be accomplished by any Brønsted acid. Subsequent experimental studies by other research groups support the mechanism proposed by Batista and co-workers for the reduction of PyH⁺ on Pt electrode. These studies demonstrate
that PyH\(^+\) behaves similar to many other weak acids: the proton bound to the nitrogen is reduced to a surface hydride.

Keith and Carter proposed an alternative heterogeneous mechanism for Py-catalyzed CO\(_2\) reduction on p-GaP photoelectrodes\(^{26,32,33}\). In this mechanism, adsorbed Py is converted into an active catalytic species, namely adsorbed dihydropyridine (DHP). Keith and Carter found that the homogeneous two-electron reduction of Py to DHP has a moderate reduction potential (-0.72 V vs. SCE\(^{26}\)). This finding suggests that DHP might form under electrochemical conditions (-0.58 V vs. SCE applied potential on Pt\(^{15}\)). In subsequent work by Carter and co-workers, the adsorption of Py and DHP was computationally investigated and both were predicted to adsorb on the solvated GaP(110) surface at room temperature\(^{34}\), suggesting that the two-electron reduction occurs on the surface. Keith and Carter also computed the heterogeneous two-electron reduction potential for reducing adsorbed Py to adsorbed DHP and found a very similar value to the homogeneous one (-0.71 V vs. SCE\(^{32,33}\)).

An earlier theoretical investigation of the interaction between water and the GaP(110) surface by Muñoz-García and Carter showed that water dissociation is thermodynamically favored on this surface and the first adsorbed monolayer of water is most stable as half-dissociated. This study also showed that water dissociation on this surface generates hydride-like species bound to phosphorus adsorption sites\(^{35}\). Based on these results, Keith and Carter hypothesized that adsorbed Py could be reduced to adsorbed DHP by adsorbed hydride-like species and protons in solution\(^{32,33}\). In this thesis work, we further investigate water dissociation at the GaP/H\(_2\)O interface in a combined experimental-theoretical study (Chapter 3). We also investigate the stability and reactivity of the surface hydride species involved in the mechanism.
proposed by Keith and Carter (Chapter 5 and Chapter 7). Once formed, adsorbed DHP could catalyze CO$_2$ reduction by hydride and proton transfer. The overall mechanism for the reduction of CO$_2$ to formic acid proposed by Keith and Carter is depicted in Figure 1.3. Contemporaneously with the Keith-Carter hypothesis, Bocarsly and co-workers reported experiments suggesting that DHP is not a reduction product in this system and further cannot act as a reducing agent for CO$_2$. However, these experiments were not performed in the presence of the p-GaP photocathode that Keith and Carter hypothesize plays a role in the catalysis.

![Figure 1.3 Mechanism proposed by Keith and Carter for heterogeneous pyridine (Py)-catalyzed CO$_2$ reduction on p-GaP photoelectrodes](image)

In 2014, after this thesis work had already begun, DHP was proposed as the active catalyst in a homogeneous mechanism by Musgrave and co-workers. In their proposed mechanism (Figure 1.4), PyH$^+$ is reduced to the previously proposed 1-PyH$^-$ radical, which is further reduced to DHP via transfer of both an electron and a proton. Once formed, DHP transfers protons and hydrides to CO$_2$ in a way similar to the heterogeneous mechanism proposed earlier by Keith and Carter (Figure 1.3). We have already presented the numerous
studies ruling out PyH\(^+\) reduction to 1-PyH\(^-\) on Pt electrodes; however, Musgrave and co-workers argued that the photoexcited electrons produced at the p-GaP photocathode are energetic enough for 1-PyH\(^-\) formation to occur. We extensively investigate this crucial aspect for the validity of the mechanism proposed by Musgrave and co-workers in this dissertation (Chapter 6). Another important aspect that can undermine the validity of this mechanism is that, as noted for the mechanism proposed by Bocarsly and co-workers, this homogeneous mechanism is not entirely consistent with the experimental observations discussed in the previous section. In fact, a homogeneous mechanism does not require catalytic assistance from the electrode surface and hence cannot explain the previously discussed electrode dependence of underpotentials and product selectivity. The role of the electrode surface is also the object of an investigation presented in Chapter 6.

Figure 1.4 Homogeneous mechanism proposed by Musgrave and co-workers for solvated dihydroyridine (DHP) formation on p-GaP photoelectrodes.\(^{36}\) Pyridinium (PyH\(^+\)) is reduced to the 1-pyridinyl radical (1-PyH\(^-\)), which further reacts to form DHP in solution. DHP is the active catalyst that transfers protons and electrons to CO\(_2\).
1.4 Thesis Outline

In this dissertation, we employ quantum-mechanics-based simulations to shed light on the mechanism of Py-catalyzed CO₂ reduction on p-GaP photocathodes in the system developed by Bocarsly and co-workers. In Chapter 2, we present an overview of the quantum-mechanics-based methods used in this work, and we also provide our detailed computational approach in each subsequent chapter.

In Chapter 3, we present a thorough study of the GaP(110)/H₂O interface conducted in collaboration with Professor Bruce E. Koel’s research group at Princeton University. As explained in further detail in that chapter, GaP(110) represents both the most stable and most active surface of GaP. We find that water dissociation is favorable under experimental conditions, in agreement with a previous study by our group and with the experimental results obtained by our collaborators. This is an important result because surface-adsorbed species deriving from water dissociation play an active role in the mechanism proposed by Keith and Carter (Figure 1.3). Furthermore, this characterization of the GaP(110)/H₂O interface allows us to develop a proper computational model of the electrode surface, which is necessary to obtain accurate results in the subsequent chapters.

In Chapter 4, we investigate the interaction of various relevant species with the GaP(110) surface, which is simulated with both periodic slab and solvated cluster models. Our calculations show that Py and DHP favorably adsorb at room temperature, in agreement with a previous study by our group. We also find that CO₂ and PyH⁺ adsorption is not favorable, thus suggesting that an adsorbed catalyst might be needed to shuttle electrons to CO₂ and such role cannot be played by PyH⁺. This study not only provides useful mechanistic insights, but it also serves as a
validation for the solvated cluster model of the GaP(110) surface employed in subsequent chapters to calculate relevant thermodynamic properties of adsorbed species as well as heterogeneous reaction energetics.

In Chapter 5, we investigate the stability of the adsorbed protons generated at the GaP(110)/H₂O surface upon water dissociation. These protons have been proposed to develop a hydride character and directly participate to the formation of the active catalyst adsorbed DHP in previous studies by our group.32,33,35 We use our solvated cluster model of the GaP(110) surface to calculate the adsorbed proton pKₐ under typical experimental conditions. We then compare the adsorbed proton pKₐ to the computed pKₐ of other relevant species in this system. Based on these data, we establish that the adsorbed protons are very stable, suggesting that they will be present on the surface and available to be reduced to surface hydrides, which could then react as proposed by Keith and Carter.32,33

In Chapter 6, we investigate the role of PyH⁺ and the surface in the catalytic CO₂ reduction mechanism. As discussed in section 1.3.1, experimental results on various electrode materials suggest that both PyH⁺ and the surface might be playing a critical role in the catalytic mechanism. In this study, we use our solvated cluster model and accurate periodic boundary condition calculations to determine whether the previously proposed PyH⁺ to 1-PyH⁻ reduction step could occur by transfer of photoexcited electrons from the p-GaP photocathode. For this purpose, in addition to performing electron density difference and charge analyses, we compare the computed conduction band minimum (CBₘᵢₙ) of the GaP(110) surface to the computed reduction potentials of various PyH⁺ reduction pathways. Based on these results, we conclude that PyH⁺ is more favorably reduced to an adsorbed hydrogen atom and adsorbed Py, which are
the reactants required for adsorbed DHP formation in the mechanism proposed by Keith and Carter.\textsuperscript{32,33} We also provide strong evidence to support the hypothesis that the electrode surface is directly involved in the catalytic mechanism, based on the experimentally observed difference in activity between the GaP(110) and GaP(111) surfaces\textsuperscript{38} and various thermodynamic properties we compute for the two surfaces.

In Chapter 7, we study the thermodynamics and kinetics of the hydride transfer steps hypothesized by Keith and Carter in their proposed mechanism (\textit{i.e.}, surface hydride transfer to adsorbed Py to form adsorbed DHP, and hydride transfer from adsorbed DHP to CO\textsubscript{2}).\textsuperscript{32,33} In particular, we use our solvated cluster model of the GaP(110) surface to compute relevant thermodynamic hydricities and reaction energetics. We find that the transfer of surface hydrides either directly to CO\textsubscript{2} or to adsorbed Py for DHP formation is kinetically hindered, although the thermodynamic hydricities support the overall mechanism proposed by Keith and Carter. We conclude that an intermediate that does not require surface hydride transfer in order to form must act as a catalyst in this system. Adsorbed deprotonated DHP (2-PyH\textsuperscript{-}) is a promising candidate as an alternative catalytic intermediate for CO\textsubscript{2} reduction, according to our computed thermodynamic hydricities.

In Chapter 8, we introduce and investigate two alternative catalytic intermediates: an adsorbed 2-pyridinyl radical (2-PyH\textsuperscript{•}) and adsorbed 2-PyH\textsuperscript{-}. We investigate the stability of these intermediates and the thermodynamic driving force for forming them, based on the GaP(110) CB\textsubscript{min} and the computed reduction potentials for their formation \textit{via} either adsorbed Py reduction or solvated PyH\textsuperscript{+} reduction. We find that adsorbed 2-PyH\textsuperscript{-} is more favorably formed than adsorbed 2-PyH\textsuperscript{•}, which is an expected result given the closed-shell nature of 2-PyH\textsuperscript{•}. However,
adsorbed \( o \)-DHP formation will compete with adsorbed \( 2 \)-PyH\(^-\) formation. Based on these results, we proceed to compute and compare the reaction energetics for hydride transfer to \( \text{CO}_2 \) from adsorbed \( 2 \)-PyH\(^-\) and \( o \)-DHP. We find that \( 2 \)-PyH\(^-\) reaction with \( \text{CO}_2 \) has a much lower activation energy and is more thermodynamically favorable, consistent with the thermodynamic hydricities computed in Chapter 7. We therefore conclude that if \( 2 \)-PyH\(^-\) formation is kinetically viable and this species has a long-enough lifetime before being protonated, then \( 2 \)-PyH\(^-\) is a plausible catalytic intermediate in the mechanism of Py-catalyzed \( \text{CO}_2 \) reduction.

We conclude this work with Chapter 9, where we summarize our findings and their implications for the mechanisms of Py-catalyzed \( \text{CO}_2 \) reduction on p-GaP photocathodes.

1.5 References


Chapter 2

Theory and Methods†

2.1 Time-Independent Schrödinger Equation for a Multi-Electron System

In this work, we use quantum mechanical methods to determine relevant properties for the catalytic system under study. To this end, one aims to determine the ground state of each system and its total energy by solving the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi$$  \hspace{1cm} (2.1)

where $\psi$ is the wave function, $E$ is the total energy of the system, and $\hat{H}$ is the Hamiltonian operator given by

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}$$  \hspace{1cm} (2.2)

where $\hat{T}_e$ is the kinetic energy operator for the electrons, $\hat{T}_n$ is the kinetic energy for the nuclei, $\hat{V}_{ne}$ is the operator for the potential energy of attraction between nuclei and electrons, $\hat{V}_{ee}$ is the operator for the potential energy of repulsion between electrons, and $\hat{V}_{nn}$ is the operator for the potential energy of repulsion between the nuclei. The Hamiltonian operator in Eq. (2.2) is extremely complex due to the pairwise attraction and repulsion terms describing the correlated motion of nuclei and electrons; because of these terms, the Schrödinger equation for a multi-
electron system can only be solved by employing approximate methods. Some of these methods are discussed in the following subsections.

2.1.1 Born-Oppenheimer Approximation

The electrons move much faster than the nuclei because they have much lighter mass. We therefore can regard the nuclei as fixed while the electrons are moving. Under this assumption, the Born-Oppenheimer approximation allows us to neglect the coupling between electronic and nuclear motion. The nuclear positions consequently become simple parameters in the Schrödinger equation. The term $\hat{T}_n$ can be removed from Eq. (2.2), resulting in the following electronic Hamiltonian expressed in atomic units that includes the nuclear repulsion term:

$$\hat{H}_{el} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$$  \hspace{1cm} (2.3)

where $i$ and $j$ are electron indices; $\alpha$ and $\beta$ are nuclear indices; $\nabla_i^2$ is the Laplacian operator; $Z_\alpha$ and $Z_\beta$ are atomic numbers; and $r_{i\alpha}$, $r_{ij}$, and $r_{\alpha\beta}$ are distances between different particles. The first, second, third, and fourth terms on the right-hand side of Eq. (2.3) correspond respectively to the operators $\hat{T}_e$, $\hat{V}_{ne}$, $\hat{V}_{ee}$, and $\hat{V}_{nn}$ from Eq. (2.2). The resulting electronic Schrödinger equation is

$$\hat{H}_{el} \psi_{el} = E_{el} \psi_{el}$$  \hspace{1cm} (2.4)

where the only variables are the electronic coordinates, while the nuclear positions are simply parameters.
2.1.2 Variational Principle

The electronic Schrödinger equation (Eq. (2.4)) cannot be solved exactly for a multi-electron system due to the inter-electronic repulsion term. Thus, the most important approximation methods for solving Eq. (2.4) are based on perturbation theory and the variational principle. Here, we will only focus on the variational principle, which lies at the foundation of the quantum-mechanical methods employed in this work. The variational principle dictates that any trial electronic wave function $\psi_{\text{trial}}$ has an energy higher or equal to the exact energy $E_0$:

$$\frac{\int \psi_{\text{trial}}^* \hat{H} \psi_{\text{trial}} d\tau}{\int \psi_{\text{trial}}^* \psi_{\text{trial}} d\tau} = E[\psi_{\text{trial}}] \geq E_0 \quad (2.5)$$

The best trial wave function therefore can be generated by minimizing the energy with respect to the parameters the wave function depends on.

2.1.3 Pauli Principle and Slater Determinant

A first trial electronic wave function for a multi-electron system can be built simply as the product of mono-electronic wave functions, referred to as a Hartree product:

$$\psi_{\text{Hartree}} = \Phi_1(1) \Phi_1(2) \ldots \Phi_N(N) \quad (2.6)$$

where $N$ is the total number of electrons and $\Phi_i$ are monoelectronic wave functions given by the product of a spatial orbital and a spin function, which, for the sake of simplicity, are not explicitly defined here and in the following. However, such an approximate wave function is not antisymmetric with respect to the interchange of any two electrons and thus violates the Pauli exclusion principle. An antisymmetric wave function is achieved by organizing the monoelectronic wave functions $\Phi_i$ in a Slater determinant:

$$\psi_{\text{Slater}} = \Phi_1(1) \Phi_1(2) \ldots \Phi_N(N)$$

However, such an approximate wave function is not antisymmetric with respect to the interchange of any two electrons and thus violates the Pauli exclusion principle. An antisymmetric wave function is achieved by organizing the monoelectronic wave functions $\Phi_i$ in a Slater determinant:
\[ \psi_{SD} = \frac{1}{\sqrt{N!}} \begin{pmatrix} \Phi_1(1) & \Phi_2(1) & \ldots & \Phi_N(1) \\ \Phi_1(2) & \Phi_2(2) & \ldots & \Phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \Phi_1(N) & \Phi_2(N) & \ldots & \Phi_N(N) \end{pmatrix} \]  

(2.7)

2.1.4 The Hartree-Fock Method and its Limitations

The Hartree-Fock (HF) method uses the variational principle (Eq. (2.5)) to determine the optimal single Slater determinant wave function \( \psi_{SD} \), finding an approximate solution of the electronic Schrödinger equation (Eq. (2.4)) for a multi-electron system. The total energy of a Slater determinant calculated using the electronic Hamiltonian from Eq. (2.3) is given by

\[ E[\psi_{SD}] = \sum_i h_i + \frac{1}{2} \sum_{i,j}(J_{ij} - K_{ij}) + V_{nn} \]  

(2.8)

where \( h_i \) corresponds to the kinetic energy of one electron and the potential energy of attraction to the nuclei; \( \frac{1}{2} \sum_{i,j}(J_{ij} - K_{ij}) \) is the energy contribution derived from electron-electron repulsion where \( J \) and \( K \) represent respectively Coulomb and exchange integrals, and \( V_{nn} \) is the energy contribution derived from nuclear repulsion. To find the best Slater determinant wave function \( \psi_{SD} \), we minimize the total energy \( E \) with respect to the mono-electronic wave functions \( \Phi_i \).

Such a minimization procedure is carried out by solving a set of equations called the HF equations:

\[ \hat{F}\Phi_i = \epsilon_i \Phi_i \]  

(2.9)

where the mono-electronic Fock operator \( \hat{F} \) is equal to

\[ \hat{F}_i = \hat{h}_i + \sum_j (\hat{J}_{ij} - \hat{K}_{ij}) \]  

(2.10)

and the relationship between the total energy \( E \) and the eigenvalues of the Fock operator \( \epsilon_i \) is
\[ E[\psi_{SD}] = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i,j} (j_{ij} - K_{ij}) + V_{nn} \]  \hspace{1cm} (2.11)

The HF equations are solved through an iterative self-consistent field (SCF) procedure because the Fock operator depends on its own eigenvectors, \( i.e., \) the mono-electronic wave functions \( \Phi_i \).

The second term on the right-hand side of Eq. (2.8) is zero whenever two electrons with the same spin occupy the same spatial orbital, which has two important implications. First, the self-interaction error is eliminated \( i.e., \) the electron is not allowed to interact with itself. Second, the motion of electrons with the same spin is correlated in the sense that the Pauli Exclusion Principle demands that such electrons are never found in the same point in space. The permutational antisymmetry of the wave function demanded by Pauli Principle gives rise to so-called exchange interactions and their associated repulsion energies \( K_{ij} \) in Eq. (2.8). As they appear with a negative sign in the energy expression, they act to minimize the overall electron-electron repulsion.

The exact, nonlocal exchange contribution to the energy from HF theory is often used to improve the results from density functional theory (DFT), which is presented in the next section and represents the main computational method employed in this work. On the other hand, HF theory does not correlate the motion of the electrons beyond the same-spin correlation of the exchange interaction; the repulsive potential felt by each electron is simply based on the average location of the other electrons rather than the instantaneous ones, regardless of their spin. This approximation, referred to as the mean-field approach, is the main limitation of the HF method. Electron correlation therefore must be introduced into the model to achieve higher accuracy, which is the essence of the so-called post-HF methods. However, the discussion of these
methods is beyond the scope of this work, as none of the results presented in the following were obtained with such methods.

2.2 Density Functional Theory

DFT greatly simplifies the problem of solving the Schrödinger equation for multi-electron systems by using as the main descriptor the electron density instead of the wave function; the latter depends on a much larger number of variables (4\(N\) variables for a system of \(N\) electrons). The electron density depends only on three spatial variables but in principle contains all of the necessary information to calculate all ground-state properties. Two theorems, both proven by Hohenberg and Kohn, are at the foundation of DFT. The first theorem states that the non-degenerate ground-state electron density uniquely determines the external potential, \(\varepsilon\), generated by the nuclei, acting on the electrons. Thus, the system Hamiltonian, wave function, and energy, as well as other molecular electronic properties, in principle can be determined from the electron density. This first theorem can also be expressed by stating that the ground-state electronic energy \(E_0\) is a unique functional of the electron density \(\rho\):

\[
E_0[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \tag{2.12}
\]

where the functional \(E_0\) has been decomposed into a kinetic energy density functional (KEDF) \(T\), a nuclear-electron attraction functional \(V_{ne}\) (for cases in which this is the only external potential), and an electron-electron repulsion functional \(V_{ee}\). \(T\), \(V_{ne}\), and \(V_{ee}\) are all molecular electronic quantities that can be determined from the wave function and therefore are also functionals of \(\rho\). The second theorem demonstrates that a variational principle analogous to the one used in wave-function-based methods applies also to the electron density: the energy calculated as a functional of the approximate density is an upper bound to the ground-state energy of the system. In
principle, this second theorem provides us with a guiding principle to determine the best \( \rho \) and thus find \( E_0 \). However, only the relationship for calculating the functional \( V_{ne} \) from \( \rho \) is known, and a practical way to calculate \( T, V_{ee} \), and the overall \( E_0 \) from \( \rho \) is not given. Furthermore, it is not clear how \( \rho \) can be calculated without having to first solve the Schrödinger equation and determine the wave function. Thus, Hohenberg-Kohn DFT did not represent a practical improvement over wave-function-based methods.

One approach to overcome this issue is orbital-free density functional theory (OFDFT). In this approach, \( V_{ne} \) and the Coulomb part of \( V_{ee} \) are calculated from their classical electrostatic expressions while different KEDFs \( T \) can be used. The simplest is the Thomas-Fermi (TF) KEDF, which is based on the known expression for the uniform electron gas and is essentially the “local density approximation” for the kinetic energy.\(^{7-9} \) Alternatively, the semilocal (gradient-dependent) von Weizsäcker (vW) KEDF can be used,\(^{10} \) which is exact for a single orbital, or combinations of TF and vW.\(^{11-16} \) The most accurate KEDFs are fully nonlocal (e.g., the Wang-Govind-Carter (WGC),\(^{17} \) the Huang-Carter (HC),\(^{18} \) the WGC decomposition,\(^{19} \) and the enhanced-vW WGC\(^{20} \) KEDFs). The exchange part of \( V_{ee} \) can also be derived from the expression for the uniform electron gas, referred to as the local density approximation (LDA).\(^{21} \) However, the accuracy and general applicability of OFDFT are still limited, with further progress needed to be able to use OFDFT for chemistry applications. This is a highly desirable goal because it would allow us to take full advantage of the fact that DFT is centered on \( \rho \), which depends only on three spatial variables.
2.2.1 Kohn-Sham Density Functional Theory

In 1965, Kohn and Sham developed Kohn-Sham density functional theory (KSDFT),\textsuperscript{22} which was necessary to make DFT a practical, accurate, and generally applicable alternative to wavefunction-based methods. They imposed a constraint that the electron density of a fictitious system of non-interacting electrons had to be equal to the electron density of a real system where the electrons are interacting. The external potentials acting on the two systems are adjusted to ensure that the electron density is the same for both systems. The Hamiltonian for a system of non-interacting electrons is simply the sum of one-electron KS Hamiltonians $\hat{h}_i^{KS}$, and its eigenfunction is simply one Slater determinant. Kohn and Sham rewrote Eq. (2.12) by introducing a new functional $E_{xc}$:

$$E_0[\rho] = T_{ni}[\rho] + V_{ne}[\rho] + V_{ee,\text{classical}}[\rho] + E_{xc}[\rho]$$  \hspace{1cm} (2.13)

where $T_{ni}$ is the kinetic energy contribution for a system of non-interacting electrons, $V_{ne}$ is the same functional as in Eq. (2.12), $V_{ee,\text{classical}}$ is the classical electron-electron repulsion contribution, and $E_{xc}$ is the exchange-correlation functional. This latter term includes the kinetic energy correction due to the electrons interacting and the quantum mechanical corrections to the potential energy for the electron-electron interaction. Furthermore, $E_{xc}$ in principle corrects the self-interaction error, which occurs due to the relationship for $V_{ee,\text{classical}}$ allowing the electron to interact with itself. Note that this error is naturally fixed in the HF method via the exchange term ($K_{ij}$ in Eq. (2.8)).

$T_{ni}$ on the right-hand side of Eq. (2.13) is calculated from the one-electron eigenfunctions $\vartheta_i$ of the KS operators $\hat{h}_i^{KS}$ while $V_{ne}$ and $V_{ee,\text{classical}}$ can be calculated directly from $\rho \cdot \rho$ for the fictitious system of non-interacting electrons (which Kohn and Sham constrain to be equal to $\rho$).
of the real system) is simply calculated as the sum of the squares of the (occupied) one-electron eigenfunctions \( \vartheta_i \). The eigenfunctions \( \vartheta_i \) in turn are found by using the variational principle established by Hohenberg and Kohn. This leads to a set of so-called KS equations, which have a similar form to the HF equations (Eq. (2.9)):

\[
\hat{h}_i^{KS} \vartheta_i = \varepsilon_i \vartheta_i
\]  

(2.14)

The KS equations have to be solved iteratively \textit{via} a SCF cycle due to the dependency of the eigenfunctions \( \vartheta_i \) on \( \rho \). Ideally, KSDFT would be an exact method if the relationship for calculating \( E_{xc} \) from \( \rho \) was known; however, this relationship is currently unknown. Good approximations for \( E_{xc} \) therefore are needed to get accurate estimates of \( E_0 \) and the other properties we are interested in calculating. Possible approximations for \( E_{xc} \) are discussed in the next subsection.

2.2.2 Exchange-Correlation Functionals

The LDA represents the first and simplest approximation developed for \( E_{xc} \). The LDA assumes that \( E_{xc} \) can be calculated pointwise and that the known form of \( E_{xc} \) for the uniform electron gas can be used to determine it as a function of \( \rho \) at each point in space. The generalized gradient approximation (GGA) takes into account \( \rho \) changes and therefore represents an improvement over LDA where \( E_{xc} \) depends only on the local electron density. Specifically, the GGA calculates \( E_{xc} \) as a function of both \( \rho \) and the gradient of the density \( \nabla \rho \). The Perdew-Burke-Ernzerhof (PBE) functional,\textsuperscript{23} one of the many GGA functionals available, was employed in this thesis for the periodic boundary condition (PBC) calculations. Finally, hybrid functionals are obtained \textit{via} a combination of LDA or GGA functionals with exact exchange from HF theory. The exact exchange inclusion typically improves the calculated results with respect to using
LDA or GGA functionals, as it corrects at least part of the self-interaction error responsible for excessive electron delocalization. The B3LYP hybrid functional\textsuperscript{24–26} was used for all homogeneous phase and cluster model calculations performed in this work. Another way to introduce some exact exchange, and thus partly correct the self-interaction error, is to employ the DFT+U method,\textsuperscript{27–29} which was not used in this work.

2.3 \textit{Simulation of Condensed Matter}

As discussed in the introduction, this work focuses on unravelling the mechanism of CO\textsubscript{2} reduction on a semiconductor surface. Thus, the ability to properly simulate crystal surfaces was essential. We employed two different approaches to simulate this type of system. These approaches are presented in the following two subsections with their advantages and limitations.

2.3.1 \textit{Periodic Boundary Condition Calculations}

A crystal can be represented as the repetition of a unit cell, which is translated by the lattice vectors to generate the three-dimensional periodic system. In this environment, the electrons are subject to a periodic potential $U(r)$ generated by the nuclei and with the same periodicity as the crystal lattice so that

$$U(r + R) = U(r) \quad (2.15)$$

for all Bravais lattice vectors $R$. In the independent-particle model, the states allowed for the electrons subject to $U(r)$ in a crystal can be found by solving a Schrödinger equation with the following one-electron Hamiltonian:

$$\hat{H}_U = -\frac{1}{2} \nabla_i^2 + U(r) \quad (2.16)$$
The eigenstates of $\hat{H}$ have special properties due to the periodicity of $U(r)$. Specifically, Bloch’s theorem\textsuperscript{30} dictates that the eigenstates of $\hat{H}$ have the form of a plane wave $e^{ikr}$ multiplied by a function with the periodicity of the crystal $u_{nk}(r)$:

$$\psi_{nk}(r) = e^{ikr} u_{nk}(r)$$  \hspace{1cm} (2.17)

where $u_{nk}(r + R) = u_{nk}(r)$. $u_{nk}(r)$ can be expanded into a basis set of plane wave basis functions, resulting in

$$u_{nk}(r) = \sum G c_G e^{iGr}$$  \hspace{1cm} (2.18)

$$\psi_{nk}(r) = \sum G c_{G+k} e^{i(G+k)r}$$  \hspace{1cm} (2.19)

where $G$ is a general reciprocal lattice vector. The wave function form dictated by Bloch’s theorem has the great advantage of only needing to solve the Schrödinger equation for the electrons in the unit cell rather than for the infinite number of electrons in the crystal. On the other hand, both the wave functions $\psi_{nk}(r)$ and their eigenvalues, which give the sets of energies called bands, vary continuously with $k$. In principle, we therefore would have to solve an infinite number of Schrödinger equations to generate a complete electronic band structure. However, the variation of energy with $k$ is typically small, and a limited number of $k$-points is enough to compute the electronic band structure and other properties via numerical interpolation and integration.

Another issue is that there is an infinite number of vectors $G$. An infinite basis set of plane waves $e^{iGr}$ therefore is in principle necessary for the description of $\psi_{nk}(r)$. However, the coefficients $c_G$ tend to take on smaller values as $G$ increases; plane wave basis sets thus are typically truncated at a certain kinetic energy cutoff $E_{cut}$ (expressed in eV) given by
\[ E_{\text{cut}} = \frac{1}{2} G_{\text{max}}^2 \]  

where \( G_{\text{max}} \) is the highest value of \( G \) chosen. Both \( E_{\text{cut}} \) and the number of k-points used in a PBC calculation need to be carefully chosen via convergence tests. In this work, these parameters were chosen so that the total energy was converged to within 1 meV per atom.

The application of PBC calculations and plane wave basis sets is not limited to bulk materials characterized by three-dimensionality. Systems with lower dimensionality can be simulated by introducing vacuum regions of proper size in the unit cell. We simulated periodic crystal surfaces by introducing a vacuum region to separate different slabs in the direction perpendicular to the surface and we ensured that the vacuum region was thick enough to avoid interaction between the periodic images of the surface. When we had to simulate isolated molecules, which are not characterized by any periodicity, we placed the molecule in a unit cell large enough to avoid interaction between the periodic images of the molecule in all three directions.

DFT calculations with PBC calculations are a powerful tool overall for the simulation of bulk materials and surfaces because they properly account for the periodicity of these systems. However, these calculations present three main limitations. First, electrostatic interactions in a periodic system are evaluated with a method called Ewald summation, which converges only for unit cells with net zero charge. Thus, the simulation of charged system requires the introduction of a uniform background charge, which deviates from the actual distribution of counter-charges in the real system and can thus lead to artifacts. Second, up to the point when this work was first undertaken, implicit solvation models (section 2.5.1) were not readily accessible in the Vienna Ab initio simulation package (VASP),\(^{31-33}\) the software employed in this work for PBC
calculations. Thus, solvation effects could only be simulated via the addition of explicit water molecules. Third, the use of more accurate methods such as hybrid DFT or post-HF methods is prohibitively expensive for systems characterized by large unit cells. Thus, our PBC calculations were only conducted using pure DFT functionals, which lack exact exchange and are thus affected by the self-interaction error previously discussed.

2.3.2 Embedded Cluster Models

An alternative way to simulate a crystal surface is to use a cluster model consisting of a limited number of atoms placed in the lattice sites of the crystal. This approach has the great advantage that allows one to simulate crystal surfaces with refined quantum chemistry methods typically restricted to molecules, but it also presents the drawback that artifacts might arise due to boundary effects. One can use different types of embedding schemes to minimize such effects, depending on the class of material under study. In the case of metals, which are characterized largely by delocalized electrons, complex embedding schemes are required.\textsuperscript{34} In the case of ionic materials, point charge embedding schemes are sufficient to account for long range electrostatic interactions in the infinite crystal.\textsuperscript{35} Finally, in the case of covalent solids, capping atoms are typically employed to avoid artifacts due to dangling bonds.\textsuperscript{35} Another relevant factor that must be considered when using cluster models is the size of the cluster. The size must be chosen based on the simulation purpose for the cluster, and it is important to verify that the cluster is a proper model of the surface. This can be done either via a convergence test of relevant properties with respect to the cluster size or via benchmarking such properties calculated with the cluster model against the same properties calculated with a periodic model of the surface.
In this work, we used cluster models extensively to simulate the GaP(110) surface. GaP is a covalent semiconductor material, and we employed capping hydrogen atoms to saturate the dangling bonds in the cluster model. We chose to use a cluster model, in addition to a periodic model of the surface, because it allows us to 1) simulate charged species without incurring any artifact due to a uniform background charge; 2) easily employ a well-vetted continuum solvation model; and 3) efficiently use hybrid DFT with exact exchange, which is particularly important for certain calculations (e.g., activation energy calculations for charge transfer reactions). The size of the cluster was chosen so that it would have a large enough surface area to simulate adsorption for all of the relevant species in the system under study and all of the relevant reactions. The GaP(110) cluster model employed in this work was benchmarked against a GaP(110) periodic cluster model by calculating adsorption energies of relevant intermediates. The two data sets were found to agree overall (see Chapter 4 and Ref. 36).

2.4 $G_0W_0$ Method for Band Gap Computation of Semiconductors

The ability to accurately evaluate the band gap and related electronic properties of materials for energy applications is crucial when studying them. KSDFT, as a ground-state theory, is not suitable for the accurate calculation of the band gap, and the band gap derived from KSDFT one-electron eigenvalues should not in principle be compared to experimental gaps. Moreover, KSDFT using LDA or GGA $E_{xc}$ functionals severely underestimate the band gap because of the self-interaction error that occurs due to their lack of exact exchange. Better agreement with experimental results can be found when re-introducing some exact exchange via hybrid $E_{xc}$ functionals or the DFT+U method, although the formalism used in such calculations is still not consistent with the way band gaps are experimentally measured (vide infra). The GW
approximation (GWA) is a well-suited technique that can be applied to the band gap computation for solid materials and that also provides results comparable to experiments. Specifically, band gaps calculated via the GWA can be compared to the fundamental gap derived from photoemission (PE) and inverse photoemission (IPE) spectroscopy.

PE/IPE experiments are widely used to measure the band gap of semiconductors. In PE experiments, electrons are emitted by the semiconductor to the vacuum via photon absorption; the binding energies of such electrons, which correspond to the material ionization potentials (IPs), are calculated from the energy differences between the absorbed photons and emitted electrons. In IPE experiments, electrons are absorbed by the semiconductor and photons are emitted; the energy differences between the absorbed electrons and emitted photons correspond to the material electron affinities (EAs). The band gap then can be determined from the difference between the lowest IP from the PE experiment and the highest EA from the IPE experiment. The band gap thus measured is typically referred to as the fundamental (IP-EA) or electronic band gap. Alternatively, the band gap can be determined from the optical absorption spectrum of the material. The obtained band gap is typically referred to as the optical band gap, corresponding to a neutral excitation of an electron from the valence band maximum to the conduction band minimum. The difference between the fundamental band gap and optical band gap is the exciton binding energy (i.e., the interaction energy between the hole in the valence band and the excited electron in the conduction band created when the semiconductor undergoes photoexcitation). The exciton binding energy is typically small in inorganic semiconductors, so the fundamental gap estimated with GWA is considered a good approximation to the optical gap.
The results of the electron removal and addition occurring in PE/IPE experiments can be described using the quasiparticle (QP) formalism. The IP and EA can be calculated as the eigenvalues of the QP equation:

$$\left(\hat{T} + \hat{V}_{ne} + \hat{V}_{ee,\text{classical}}\right)\psi_n^{QP}(r) + \int \Sigma(r,r';\epsilon_n^{QP})\psi_n^{QP}(r)\,dr = \epsilon_n^{QP}\psi_n^{QP}(r) \quad (2.21)$$

where $\Sigma$ is the self-energy operator, which is an energy-dependent operator describing all of the non-classical electron-electron interactions (which are not accounted for by the Coulomb operator $\hat{V}_{ee,\text{classical}}$). $\Sigma$ must first be defined in order to solve the QP equation. To this end, many-body perturbation theory with the one particle’s Green’s function of the system $G(r,r';t,t')$ can be used. $G(r,r';t,t')$ represents the probability of finding an electron at $r$ at time $t$, given that there was an electron at $r'$ at time $t'$. By evaluating $G(r,r';t,t')$, one can derive the QP eigenvalues needed to calculate the fundamental gap, as well as many other properties of interest. $G(r,r';t,t')$ can be evaluated starting from the known exact $G_0(r,r';t,t')$ for a reference system via Dyson’s equation:

$$G(r,r';E) = G_0(r,r';E) + \iint G_0(r,r_1;E)\Sigma(r_1,r_2;E)G_0(r_2,r';E)\,dr_1\,dr_2 \quad (2.22)$$

The Green’s function for a system of non-interacting electrons can be calculated exactly, and thus the latter is chosen as the reference system. However, the self-energy operator $\Sigma$, which is required in order to solve Dyson’s equation, is still unknown.

Hedin therefore developed a series of equations relating $\Sigma$ to the Green’s function and other relevant quantities, including the screened Coulomb interaction $W$. When solved together with Dyson’s equation in a self-consistent way, Hedin’s equations can be used to calculate $\Sigma$. However, solving these equations via a self-consistent procedure is not a practicable solution.
Hedin developed the GWA to overcome this issue, in which the expression for the self-energy is greatly simplified by retaining only the first term in the expansion of the self-energy in terms of the Green’s function and $W$:

$$\Sigma_{GW}(r, r'; t) = iG(r, r'; t)W(r, r'; t)$$

(2.23)

While the GWA makes the calculation of $\Sigma$ easier, solving Dyson’s and Hedin’s respective equations in a self-consistent way remains a computationally demanding task for systems with more than a few atoms. A more commonly used and more affordable approach is the one-shot, non-self-consistent GW method ($G_0W_0$). In the $G_0W_0$ implementation, first-order perturbation theory is used instead of the self-consistent procedure. $\Sigma$ is simply constructed from the one-electron eigenvalues and eigenfunctions of the reference state ($e.g.$, KSDFT) and then applied in the QP equation as a perturbative correction. This approach is quite accurate, as we shall show in Chapter 6.

2.5 Simulation of Solvated Systems

This work studies catalytic CO$_2$ reduction in the presence of a solution. Thus, a proper simulation of the solvent is essential for accurately studying the catalytic mechanism. There are three main methods for simulating solvation effects: implicit, explicit, and mixed solvation methods. All three methods were employed in this work. Implicit methods, which are discussed more in depth in the following subsection, simulate the solvent as a continuum medium. These models are more cost effective, but they cannot describe specific interactions ($e.g.$, hydrogen bonds, dispersion) between the solute and the solvent. Moreover, these models only account for long-range effects such as solvent polarization. Explicit methods treat the solvent molecules explicitly and thus can capture all of the specific interactions between the solvent and solute.
However, these models can be computationally prohibitive for large solutes. Mixed solvation methods explicitly treat the solvent region closer to the solute, while the remainder is implicitly treated. Thus, these models account for the specific solute-solvent interactions while also accounting for long-range effects. In this work, only the explicit method was used for PBC calculations, because implicit solvation models were not readily available in VASP when this work was first undertaken. For cluster and molecular calculations, however, we used both the implicit and mixed solvation methods depending on the system and property under investigation.

2.5.1 Implicit Solvation Models

Implicit solvation models represent the solvent as a polarizable medium characterized by a dielectric constant $\varepsilon$. Implicit solvation models are often referred to as “reaction field models,” because the charge distribution in the solvent is represented as an electric field that gets polarized by and “reacts” to the presence of the solute. The solute is placed in a cavity of proper size and shape in the continuum medium. The solvation energy ($i.e.$, the change in free energy when a species is transferred from the gas phase to the solution phase) can be divided into three components:

$$
\Delta G_{solv} = \Delta G_{cavity} + \Delta G_{dispersion} + \Delta G_{elec} \quad (2.24)
$$

$\Delta G_{cavity}$ accounts for the energy cost or the destabilization for creating a hole in the continuum medium. $\Delta G_{dispersion}$ represents the energy gain or stabilization effect due to the dispersion interactions between the solute and solvent. This term also includes the possible repulsion between the solute and solvent. Finally, $\Delta G_{elec}$ accounts for the electrostatic stabilization deriving from the solute polarizing the continuum medium, which in turn acts back on the solute.
There are five main aspects that can differ in implicit solvation models, in terms of the way in which: 1) the cavity’s size and shape are defined; 2) $\Delta G_{\text{cavity}}$ and $\Delta G_{\text{dispersion}}$ are calculated; 3) the solute charge distribution is described (e.g., point charges); 4) the solute is simulated (i.e., with quantum or classical methods); and 5) the dielectric continuum medium is described. $\Delta G_{\text{cavity}}$ and $\Delta G_{\text{dispersion}}$ are usually considered proportional to the cavity surface area, which can be calculated in various ways. Either the Poisson equation or Poisson-Boltzmann equation must be solved to evaluate $\Delta G_{\text{elec}}$. Strategies to solve these equations and other aspects are discussed in further detail below.

The Poisson equation is a second-order differential equation that dictates the relationship between the electrostatic potential $\phi(r)$, the charge density $\rho(r)$ giving rise to such a potential, and the dielectric constant of the homogeneous continuum medium $\varepsilon$ in which the charge density is embedded:

$$\nabla^2 \phi(r) = -\frac{4\pi}{\varepsilon} \rho(r) \quad (2.25)$$

In Eq. (2.25), $\varepsilon$ is a constant and therefore does not depend on position $r$. However, the solute is placed in a cavity immersed in the continuum medium as part of the continuum solvation model, which is no longer homogeneous; $\varepsilon$ then becomes a function varying in space. Under these conditions, the Poisson equation becomes

$$\nabla \varepsilon(r) \cdot \nabla \phi(r) = -4\pi \rho(r) \quad (2.26)$$

Both Eqs. (2.25) and (2.26) apply only to a case in which the solvent is characterized by zero ionic strength. If ions are present in the solvent, the Poisson-Boltzmann equation must be used instead:
\[ \nabla \varepsilon(r) \cdot \nabla \phi(r) - \varepsilon(r) \lambda(r) \kappa^2 \frac{k_B T}{q} \sinh \left[ \frac{q \phi(r)}{k_B T} \right] = -4\pi \rho(r) \] (2.27)

where \( \lambda(r) \) is a switching function that varies depending on whether the solvent ions have access to a certain position \( r \), \( k_B \) is the Boltzmann constant, \( T \) is temperature, \( q \) is the magnitude of the charge of the solvent ions, and \( \kappa^2 \) is the Debye-Hückel parameter that depends on the ionic strength of the solvent. Eqs. (2.26) and (2.27) provide us with the value of the electrostatic potential at any point in space. These values then can be used to derive the reaction field (simply defined as the difference between the electrostatic potential in the presence of a solvent and in the gas phase), which is multiplied by the charge density \( \rho(r) \) to obtain the electrostatic contribution \( \Delta G_{elec} \) of the total free energy of solvation \( \Delta G_{solv} \).

The Poisson and the Poisson-Boltzmann equations are typically solved numerically, which can be prohibitive as we approach more complex systems. One possible solution to this problem is using a cavity with a special shape that allows one to solve these equations analytically. The Born model\(^{37}\) is the simplest reaction field model and uses a spherical cavity to calculate \( \Delta G_{elec} \) for a monoatomic ion with net charge \( q \). The Kirkwood–Onsager model\(^{38,39}\) is an improvement over the Born model, as it simulates polar species and not only species characterized by a net charge with a spherical cavity. An ellipsoidal cavity can be employed within the Kirkwood–Westheimer expansion,\(^{40}\) which is better suited than a spherical cavity for most solutes. However, very few solutes are properly described by spherical or ellipsoidal cavities. These models therefore should not be used to produce quantitative results, even though they have been used in the past to qualitatively study solvation effects because of their simplicity.
Note that if the solute is simulated with quantum mechanics and the analytical $\Delta G_{elec}$ expression contains a quantity that depends on the electron density distribution (and thus the wave function), then a self-consistent reaction field (SCRF) calculation is necessary to calculate $\Delta G_{elec}$. Specifically, the calculated dipole moment of the solute will induce changes in the continuum medium, which will in turn affect the wave function of the solute and result in a different dipole moment. The net charge of a monoatomic ion does not depend on the wave function, while the molecular dipole moment does. The Kirkwood–Onsager\textsuperscript{38,39} model therefore requires us to employ a SCRF procedure.

Many more sophisticated SCRF models that employ molecular-shaped cavities have been developed in recent years. In this case, the equations can no longer be solved analytically, so numerical methods are used to solve them. We used both the Solvation Model based on solute electron Density (SMD)\textsuperscript{41} and the COnductor-like Screening MOdel (COSMO)\textsuperscript{42} solvation models in this work. The SMD model is based on the generalized Born approximation, which approximates the Poisson and Poisson-Boltzmann equations so that they can be solved analytically. The generalized Born approximation is an extension of the Born model\textsuperscript{37} to polyatomic molecules, using partial atomic charges to describe the electron density distribution in the solute. The COSMO model assumes that the continuum medium is a conductor ($\varepsilon=\infty$), which greatly simplifies the calculation of $\Delta G_{elec}$.

2.6 References


Chapter 3

Computational Characterization of the GaP(110) Surface in an Aqueous Environment‡

3.1 Introduction

In the experimental system of Bocarsly and co-workers, the GaP electrode is immersed in an aqueous solution through which CO₂ is bubbled.¹ Characterizing the electrode/solution interface is extremely important for many reasons. Water-derived species adsorbing on the electrode surface might play a role in the catalytic CO₂ reduction mechanism. Furthermore, these species might affect the band edge positions of the electrode material (i.e., the free energy of the valence band holes and the conduction band electrons), which in turn determines what redox reactions can occur under illumination. The characterization of this interface is also necessary for developing a proper computational model of the electrode surface, which will be employed in the following chapters to investigate several aspects of heterogeneous CO₂ reduction mechanisms.

In this chapter, we use periodic density functional theory (DFT) to identify relevant water configurations at the GaP/H₂O interface, and we compute a surface-adsorbate phase diagram to determine their relative thermodynamic stabilities under experimental conditions. Following previous work in our group,²³ we chose to simulate the GaP photoelectrode surface by using the non-polar (110) surface, which represents the most stable GaP surface. Non-polar surfaces, in general, are more thermodynamically stable (i.e., have a lower surface energy) than polar

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surfaces \((e.g., \text{GaP(111)})\) and normally do not undergo reconstruction.\(^4\) The higher thermodynamic stability of the \text{GaP(110)} surface has also been confirmed by experimental studies.\(^5\) Furthermore, recent experimental work from the Bocarsly group has demonstrated that the non-polar \text{GaP(110)} surface is more active towards \text{CO}_2\ reduction than the polar \text{GaP (111)} surface.\(^6\) These recent results provide another reason for focusing on the \((110)\) surface.

In this study, we employed a periodic model of the \text{GaP(110)} surface instead of a cluster model. As discussed in section 2.3.1 of Chapter 2, a periodic model is more appropriate than a cluster model for the simulation of a crystal surface but has three main limitations: 1) charged unit cells require the application of an unphysical background charge; 2) implicit solvation models are not readily available; and 3) methods more accurate than \text{DFT} with pure functionals \((e.g.,\ \text{hybrid DFT functionals})\) can be prohibitively expensive. In this study, however, such limitations do not represent a problem. First, all of the water-derived species studied herein lead to a unit cell with overall zero charge. Second, while our goal is to characterize the \text{GaP(110)} surface when exposed to water, we are interested not in long-range solvation effects but in the specific molecular structure of water adsorbed on this surface; we therefore want to explicitly model water molecules rather than using an implicit solvation model. Third, we are only interested in determining the geometry of the \text{GaP/H}_2\text{O} interface and not yet the electronic structure; more accurate methods therefore are not required.

This investigation was conducted in collaboration with the experimental group of Professor Bruce E. Koel at Princeton University. His group used ambient pressure photoelectron spectroscopy (APPES) measurements to determine the adsorbates forming when the \text{GaP(110)} surface is exposed to water.\(^7\) In this chapter, after presenting our computational approach and
results, we will briefly summarize these experimental findings and compare our results to them. We then discuss the implications of these results for the mechanism of CO$_2$ reduction in this system.

3.2 Computational Approach

3.2.1 Computational Details

We performed DFT$^{8,9}$ calculations with periodic boundary conditions to identify relevant water configurations on the GaP(110) surface and assess their associated thermodynamic stabilities. All calculations were performed using the software package Vienna Ab initio Simulation Package (VASP),$^{10–12}$ the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,$^{13}$ and default projector augmented wave (PAW) potentials$^{14}$ to describe nuclei and frozen core electrons (1s2s2p3s3p3d for Ga, 1s2s2p for P and 1s for O). We described the rest of the electrons using a plane wave basis with a kinetic energy cutoff of 800 eV. We used 6×4×1 k-point sampling based on the Monkhorst-Pack scheme.$^{15}$ The Brillouin zone was integrated using the Gaussian smearing method with smearing width equal to 0.05 eV. For the calculation of an isolated water molecule, we only sampled the Γ point with a smearing width equal to 0.001 eV. Overall, with these computational parameters, the total energy was converged to within 1 meV/atom.

We used the same model for the GaP surface as that used in previous work by our group (a seven-layer slab generated from a 1×2 unit cell of the GaP(110) surface, resulting in four GaP formula units in each layer).$^2$ We modeled different water coverages, defined as the number of adsorbate molecules divided by the number of Ga adsorption sites per surface, ranging from 0.25 to 2 monolayers (ML). Adsorbates were symmetrically placed on both sides of the slab to eliminate artificial net dipoles. A vacuum space larger than 20 Å was inserted in between slabs to
avoid interaction of periodic images along the surface normal direction. During geometry optimization, we allowed all the adsorbate atoms and the four outermost GaP layers to relax while keeping the cell shape and volume fixed. We also kept the three middle layers frozen in order to capture the effects arising from the bulk regions of a semi-infinite crystal. Finally, we verified that our calculated structures are minimum-energy structures by calculating the corresponding vibrational frequencies and verifying that none had an imaginary frequency. We calculated only the frequencies of the atoms that were allowed to relax. For the isolated water molecule, we also computed the frequencies associated with rotational and translational modes using the ideal gas, rigid rotor, and harmonic oscillator approximations. The vibrational frequencies were computed from a numerical Hessian calculated using displacements of ±0.02 Å and analytic gradients.

3.2.2 Adsorbate-Surface Phase Diagram Computation

We computed a phase diagram for water on the GaP(110) surface to determine the most stable water structures on this surface under experimental conditions (ultrahigh vacuum (UHV) and room temperature). To construct the phase diagram, we considered the variation of the room-temperature adsorption free energy of all the modeled water configurations with respect to the water chemical potential shifting from water-poor to water-rich conditions (i.e., from low to high water pressures at the surface). Using the chemical potential, we can simulate different water conditions at the surface. Water-rich (water-poor) conditions at the surface are represented by gas (liquid) phase water in a reservoir in contact with the surface, because at room temperature gaseous (liquid) water is unstable (stable) in the reservoir. More information regarding the use of the water chemical potential in constructing the phase diagram can be found in previous work in which a similar diagram was computed for a different surface.16
We calculated the adsorption free energy, $\Delta \Omega$, dependent on the water chemical potential, $\mu_w$, using the following equation:

$$\Delta \Omega(T, p) = \frac{1}{2} (G_{\text{slab}+nW} - G_{\text{slab}} - n\mu_w(T, p))$$

(3.1)

$G_{\text{slab}+nW}$ is the free energy of the GaP slab-water complex containing $n$ water molecules and $G_{\text{slab}}$ is the free energy of the bare GaP slab. Both energies include zero point energy and thermal corrections at room temperature. $n$ is the total number of water molecules adsorbed on both sides of the slab. $\mu_w$ is the chemical potential of water, which depends on temperature, $T$, and pressure, $p$. We introduce the factor $\frac{1}{2}$ because as discussed above we model adsorbates on both sides of the slab, but we are interested in the adsorption properties of one surface only. The chemical potential $\mu_w$ is shifted from water-poor to water-rich conditions using the parameter $\Delta \mu_w$, as illustrated in the following equation:

$$\mu_w = \Delta \mu_w + G_w^{\text{gas}}$$

(3.2)

$G_w^{\text{gas}}$ is the free energy of a water molecule in the gas phase and includes zero point energy and thermal corrections at room temperature. When $\Delta \mu_w$ is equal to 0 eV, $\mu_w$ is the chemical potential of water in the gas phase, which corresponds to water-rich conditions at the surface; when $\Delta \mu_w$ is equal to -0.09 eV, $\mu_w$ is the chemical potential of water in the liquid phase describing water-poor conditions at the surface. The value -0.09 eV is the difference between the experimental values of the water chemical potential in the liquid and gas phases at room temperature.\(^{17}\)
3.2.3 Water Adsorption Configurations Under Study

In order to build the phase diagram, we modeled several possible initial configurations of water, varying coverage and degree of dissociation. Coverages considered range from 0.25 ML (i.e., one water molecule per surface unit cell) to 2 ML (i.e., eight water molecules per surface unit cell), where coverage is defined as the number of adsorbate water molecules divided by the number of Ga adsorption sites per surface unit cell. For each coverage, we investigated an undissociated configuration and a dissociated configuration. Figure 3.1 displays the configurations considered for each coverage along with its respective degree of dissociation. At 0.25 ML, the one water molecule in the unit cell is dissociated heterolytically by adsorbing the hydroxide on a surface Ga atom and the proton on a neighboring surface P atom. In this way, 100% dissociation is obtained. At 0.5 ML, two water molecules are in the unit cell. We investigated the effect of dissociating one molecule, which corresponds to 50% dissociation, and then also adding an undissociated water molecule to this configuration, reaching 0.75 ML coverage with 33% dissociation. These three configurations were investigated to study whether co-adsorbed water molecules assist dissociation. Finally, we modeled 1 ML and 2 ML coverages, both with 50% dissociation within the first monolayer. These two configurations were considered in order to investigate the effect of a solvating layer (i.e., the second water monolayer) on dissociation occurring in the first monolayer. Note that the dissociated configurations considered in this work have different geometries with respect to those modeled in previous work.²
Figure 3.1 Relaxed structures of all water configurations considered in this work. Each water configuration is defined by the coverage (expressed in monolayers (ML)) and the degree of dissociation (D). Figure adapted from Ref. 7. Copyright 2015 American Chemical Society.

### 3.3 Results and Discussion

#### 3.3.1 Adsorbate-Surface Phase Diagram from Density Functional Theory

In the phase diagram (Figure 3.2), for each value of water chemical potential (i.e., water conditions at the surface), the configuration with the most negative adsorption free energy represents the most thermodynamically stable one.
Figure 3.2 Computed H$_2$O phase diagram on GaP(110) at T=298.15 K. $\Delta\Omega$ is the adsorption free energy, and $\Delta\mu_w$ is the chemical potential shift from water-rich conditions (i.e., the chemical potential of gas phase water) as illustrated in section 3.2.2. Each water configuration is defined by the coverage (expressed in monolayers (ML)) and the degree of dissociation (D). Solid lines represent undissociated configurations, and dashed lines represent dissociated configurations.

Overall, the 1 ML, half-dissociated configuration (blue dashed line in Figure 3.2) represents the most stable water configuration for both water-poor and water-rich conditions. This configuration involves the Ga-OH, P-H, and adsorbed molecular H$_2$O species observed in this work by APPES (vide infra). In addition, in this half-dissociated configuration, Ga-OH and H$_2$O species interact via hydrogen bonding (Figure 3.3), which was also observed here experimentally (vide infra).
Figure 3.3 Half-dissociated configuration of water on GaP(110) predicted by density functional theory (DFT) calculations: the proton binds to a P adsorption site while the hydroxide binds to a Ga adsorption site. An undissociated H$_2$O molecule interacts with the hydroxide via a hydrogen bond (represented by the blued dotted line).

In addition to the agreement between experimental and computational findings (vide infra), the phase diagram (Figure 3.2) yields three important results. First, we observe that adsorption of water is always favored except for the 2 ML undissociated configuration and the 0.25 ML dissociated configuration when approaching water-poor conditions. In fact, only under these conditions do the lines corresponding to these configurations fall above the black horizontal line (0 ML) representing the clean surface (i.e., the adsorption free energy becomes positive and adsorption of water in these configurations is no longer thermodynamically favored). Second, inspection of the water phase diagram reveals that for coverages larger than 0.25 ML, water dissociation is always thermodynamically favored even in water-poor conditions. In fact, each dissociated configuration (dashed lines in (Figure 3.2)) is more stable (lower free energy) than the corresponding undissociated configuration (solid lines in (Figure 3.2)), except
for the 0.25 ML case. In previous work, water dissociation was predicted to be favored only for coverages larger than 2 ML. Here we find water dissociation to be favorable at much lower coverages (0.5 ML), resulting from finding a more stable adsorption geometry for the partially dissociated configurations than was found earlier. In particular, in our current structures, an adsorbed hydroxide deriving from water dissociation is stabilized by the presence of a co-adsorbed, undissociated water molecule that promotes dissociation via hydrogen-bonding, as shown in Figure 3.3. The 0.25 ML anomaly is therefore easy to understand: dissociation is not favored at that low coverage because there are not enough water molecules on the surface to promote dissociation via hydrogen bonding. Third, relative adsorption free energy values of the 2 ML 50% D and 1 ML 50% D configurations suggest that at room temperature the formation of a solvation layer on top of the first adsorbed layer of water is not thermodynamically favored (i.e., the 2 ML 50% D configuration is higher in energy than the 1 ML 50% D configuration). This occurs because hydrogen bonds among the first and second monolayers are not strong enough to overcome the entropic contribution that drives the evaporation of the second monolayer at room temperature. In addition, this finding is consistent with the results of molecular dynamics simulations of liquid water in contact with metal surfaces reported by Limmer et al., which shows the formation of a hydrophobic water layer on the surface.

3.3.2 Comparison to Ambient Pressure Photoelectron Spectroscopy Results

X-ray photoelectron spectroscopy (XPS) can be used to study the surface chemistry of a material either in its pristine state or after some treatment (e.g., exposure to water). XPS measures the binding energy of core electrons, which is directly affected by both the local chemical environment and oxidation state of the probed atom. While XPS is traditionally employed under UHV conditions, experiments can also be conducted at pressures closer to ambient conditions in
so-called APPES. Our collaborators employed APPES to probe the binding energy change of oxygen 1s, gallium 3d, and phosphorus 2p core electrons when the GaP(110) surface is exposed to water both under UHV conditions and at higher pressures. Their experiments were conducted at 38 °C, but they confirmed in independent experiments that their results are also valid at room temperature and thus can be directly compared to our computational results.

The peak observed in the APPES O 1s spectra (Figure 3.4a) can be deconvoluted into two component peaks, which were assigned to hydroxide and molecular water adsorbed on the surface. This result was also confirmed by the presence of a peak characteristic of Ga-OH species in the APPES Ga 3d spectra (not reported here). An additional new peak appears at higher pressures (≥0.1 Torr) due to the presence of vapor phase water. Finally, a new peak (indicated by * in Figure 3.4a) is detected at 0.4 Torr and can be assigned to interacting adsorbed hydroxide and molecular water. These results overall suggest that partial water dissociation occurs at the GaP(110)/water interface. Furthermore, the water configuration likely resembles the one predicted by our computed adsorbate-surface phase diagram (Figure 3.2) and illustrated in Figure 3.3.

The APPES P 2p spectra (Figure 3.4b) corroborate these findings. Under UHV conditions, two partially resolved peaks are detected due to spin-orbit splitting. A new set of peaks (indicated by the two arrows in Figure 3.4b) with a higher binding energy appears after exposure to H₂O \textit{in situ} (i.e., at higher pressures closer to ambient pressure). These peaks are assigned to P-H surface species, which form as a result of water dissociation on the surface according to our computed phase diagram (Figure 3.2). Furthermore, the higher binding energies of these peaks suggests that charge transfer occurs from the surface P to the proton bound to it, in
agreement with previous computational work in our group predicting the formation of negatively charged hydrides when water dissociates on the surface.\textsuperscript{2}

Figure 3.4 Isothermal ambient pressure photoelectron spectroscopy (APPES) spectra from GaP(110) after exposures to H\textsubscript{2}O in ultrahigh vacuum (UHV) and \textit{in situ}. (a) O 1s spectra. Figures on the left show data acquired at 4×10\textsuperscript{-9} Torr base pressure after exposing the sample to H\textsubscript{2}O at 1×10\textsuperscript{-7} Torr. Figures on the right show \textit{in situ} measurements at the indicated pressures. (b) Normalized P 2p spectra. Figures on the left show data acquired at 4×10\textsuperscript{-9} Torr base pressure after exposing the sample to H\textsubscript{2}O at 1×10\textsuperscript{-7} Torr. Figures on the right show \textit{in situ} measurements at the indicated pressures. Bold lines are experimental data, and fine lines are fitted component contributions. Figures adapted from Ref. 7. Copyright 2015 American Chemical Society.
Overall, the APPES results confirm our predictions that the half-dissociated configuration of water is the most stable one under water-poor conditions (which correspond to the relatively low pressure conditions used in the experiments), and that this configuration is characterized by adsorbed hydroxide and molecular water interacting via a hydrogen bond (Figure 3.3). The results of this combined computational and experimental study are consistent with a number of observations of spontaneous H$_2$O dissociation on related surfaces in recent years: GaAs(100),$^{19}$ GaP(111),$^{20}$ GaAs nanowires,$^{21}$ InP(100),$^{22}$ and GaN(10$ar{1}$0),$^{23}$ as well as several recent theoretical studies on related III-V surfaces.$^{24-26}$

3.4 Conclusions

In summary, we find that water adsorption and dissociation is always thermodynamically favored on this surface if the Ga-OH species are stabilized by a hydrogen bond with an undissociated H$_2$O molecule, with 1 ML being the most thermodynamically favored coverage both under water-poor and water-rich conditions. Thus, our computational findings are in excellent agreement with the results of APPES measurements conducted under UHV and in situ at low pressure (i.e., under water-poor conditions): we predict that all the experimentally observed species are thermodynamically stable at room temperature and in water-poor conditions. Our computed phase diagram also suggests that the electrode surface will be covered by a full monolayer of half-dissociated water molecules in the photoelectrocatalytic system under study, where the GaP electrode is in contact with an aqueous solution (i.e., the electrode surface is under water-rich conditions).$^{1}$ This configuration therefore will be used in the following chapters to simulate the explicitly solvated electrode surface. Furthermore, our predictions that water will dissociate in the experimental system$^{1}$ and that hydride-like species will form on the
electrode surface offers partial validation of the CO$_2$ reduction mechanism proposed by Keith and Carter (see section 1.3.2 of Chapter 1),$^{27,28}$ given that in this mechanism surface hydrides are directly involved in the formation of the active catalyst.

3.5 References


Chapter 4

Computational Study of the Interaction of Relevant Species with the GaP(110) Surface

4.1 Introduction

In this chapter, we study the interaction of various molecules with the GaP(110) surface, which, as discussed in section 3.1 of Chapter 3, represents both the most stable and the most active GaP surface towards CO₂ reduction. The molecules under investigation are H₂O, CO₂, pyridine (Py), pyridinium (PyH⁺), and dihydropyridine (DHP). These species were considered based on the experimental conditions and the proposed mechanism on GaP electrodes. The observed catalytic performance in the experiments depends on the electrode material, thus suggesting that the electrode might be directly involved in the mechanism of Py-catalyzed CO₂ reduction. Understanding whether these molecules favorably interact with the electrode surface therefore can help us shed some light on the mechanism occurring at GaP electrodes.

We study the adsorption geometry and calculate the adsorption free energy of each species on the GaP(110) surface by using density functional theory (DFT) with both periodic and cluster models, given that these models have different advantages and limitations (section 2.3 of Chapter 2). Furthermore, this study allows us to benchmark and validate our solvated cluster model of the GaP(110) surface against results obtained with the periodic slab model. Note that a

‡ Portions of this chapter were adapted from the following papers with permission:
Reproduced in part from Lessio, M.; Riplinger, C.; Carter, E. A. Phys. Chem. Chem. Phys. 2016, 18, 26434-26443 (both main text and supplementary information) with permission from the Royal Society of Chemistry.
similar validation study was already conducted by our research group.\textsuperscript{11} However, we employ throughout this thesis work a cluster model built with a slightly different procedure, and we use a different implicit solvation model (section 4.2.2). A new validation study therefore is necessary. Furthermore, in the previous study,\textsuperscript{11} thermal corrections at room temperature were only included for the adsorption energy computed with the cluster model. In this new study, we include these corrections for results obtained with both the cluster and periodic slab models. These and other differences between the two studies are further discussed in section 4.2. Once we have established the validity of our new solvated cluster model, we then use this model to study how the presence of adsorbed explicit water molecules and surface negative charge affect the adsorption strength of the species under study. These are important effects to investigate given that the GaP photocathode in the experimental system is immersed into an aqueous solution, with a negative bias applied to it.\textsuperscript{3} Finally, we discuss the implications of the overall adsorption free energy trend for the mechanism of CO\textsubscript{2} reduction in this system. In the case of Py, we also report the results of a combined experimental and theoretical study aimed at characterizing the reactivity of Py adsorbed on GaP(110), conducted in collaboration with the group of Professor Bruce E. Koel at Princeton University.\textsuperscript{12}

4.2 Computational Approach

4.2.1 Periodic Boundary Condition Calculations

We performed all calculations using the Vienna Ab initio Simulation Package (VASP) software package\textsuperscript{13–15} and the all-electron, frozen core, projector-augmented wave (PAW) method\textsuperscript{16} within DFT\textsuperscript{17,18} with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional.\textsuperscript{19} All nuclei (Ga, P, N, C, O, and H) and frozen core electrons (1s2s2p3s3p3d for Ga, 1s2s2p for P, 1s
for N, 1s for C, and 1s for O) were simulated using the default PAW potentials within VASP.\textsuperscript{20} The rest of the electrons were simulated using a plane wave basis with 800 eV kinetic energy cutoff. We included Grimme’s D2 dispersion correction\textsuperscript{21} for all of the species under study. Including this correction was especially relevant for CO\textsubscript{2} given that this molecule typically adsorbs \textit{via} physisorption, a process dominated by dispersion interactions.

In the case of H\textsubscript{2}O and CO\textsubscript{2}, the remaining computational details are identical to those employed for the GaP(110)/water interface study presented in Chapter 3 except for the fact that here the mirrored slab model (\textit{i.e.}, built by cleaving the bulk GaP crystal so that the two surface terminations are identical and no surface dipole develops) was obtained from a bulk crystal fully relaxed with the dispersion correction (5.447 Å cell parameter \textit{versus} 5.534 Å without dispersion correction). Note that in the previous study by our group,\textsuperscript{11} a larger supercell (2x3 unit cells) was employed than the one employed in this study for H\textsubscript{2}O and CO\textsubscript{2} (1x2 unit cells). However, these molecules are both small enough that we do not expect the adsorbate periodic images to interact when using the smaller supercell.

In the case of Py, we sampled the Brillouin zone using a 2\times2\times1 k-point mesh based on the Monkhorst-Pack scheme.\textsuperscript{22} We integrated the Brillouin zone using the Gaussian smearing method and a smearing width equal to 0.05 eV. For the free Py molecule, we only sampled the \Gamma point and used a 0.001 eV smearing width. With these computational parameters, we reached a convergence of the total energy to within 1 meV per atom. We used the same mirrored slab model validated in our previous work:\textsuperscript{11} a 2\times3 supercell with a thickness of five layers for a total of 12 GaP formula units per layer. However, here the slab was obtained from a bulk crystal fully relaxed with the dispersion correction. During geometry optimization, we allowed all atoms to
relax except for the atoms in the central layer which are kept fixed in the bulk positions to simulate a semi-infinite crystal. In our model, the vacuum region in between slabs was larger than 20 Å to avoid interaction between periodic images along the direction perpendicular to the slab. We modeled adsorbed Py on both sides of the slab to avoid surface dipole formation. Finally, we placed one Py molecule per unit cell on each side of the slab corresponding to a 1/12 monolayer coverage, given that there are 12 Ga adsorption sites per surface.

To verify that the relaxed structure of Py was a minimum structure, we computed its vibrational frequency and found no imaginary frequency. Given the large number of atoms in the unit cell (142 atoms), we did not compute the frequencies associated with all the atoms. Instead, we only considered enough atoms for the zero point energy (ZPE)-corrected adsorption energy to be converged within 1 meV. This choice resulted in considering all the Py atoms, part of the atoms in the bare slab and part of the atoms in the slab with Py on top. Specifically, we considered three Ga atoms and five P atoms in the bare slab and in the slab with adsorbed Py. These were the Ga atom directly bound to the N atom of the adsorbed Py, the three P atoms directly bound to this Ga atom, the nearest neighbors and next-nearest neighbors to these three P atoms within a 4 Å radius from the Py molecule. The frequencies were computed from a numeric Hessian obtained using analytic gradients and ±0.02 Å displacements. These frequencies were also used to calculate ZPE, enthalpic, and entropic corrections using the ideal gas and the harmonic oscillator approximations. For the free Py molecule, we used also the rigid rotor approximation to account for rotational mode contributions.

In the case of DHP, we used the same computational details and slab model as the one used for Py. The supercell was characterized by a large number of atoms (146), thus we again
had to limit the number of atoms included in the frequency calculation. For this purpose, we used
the same criterion applied in the Py study. This criterion led us to consider five Ga atoms and
five P atoms in addition to all of the atoms belonging to the DHP molecule. Note that periodic
boundary condition calculations were not used to study PyH\(^+\) adsorption; this would lead to a
positively charged supercell, which would then require the application of an unphysical uniform
background charge to allow for the ion-ion Ewald sum to converge.

We computed the adsorption free energy \(G_{ads}(x)\) at \(T=298.15\) K per surface for each
species \(x\) using the following equation:

\[
G_{ads}(x) = \frac{1}{2}(G_{slab+x} - G_{slab} - 2G_x)
\]

(4.1)

where \(G_{slab+x}\) is the free energy of species \(x\) adsorbed on both sides of the mirrored slab, \(G_{slab}\)
is the free energy of the bare mirrored slab, \(G_x\) is the free energy of species \(x\) in the gas phase,
and \(x\) is either H\(_2\)O, CO\(_2\), Py, or DHP. The factor \(1/2\) is required to calculate the adsorption free
energy per surface given that adsorbates are modeled on both sides of the slab.

4.2.2 Solvated Cluster Model Calculations

All calculations were performed using the ORCA software package\(^{23}\) and DFT\(^{17,18}\) geometry
optimizations were carried out with the B3LYP XC functional\(^{24-26}\) using the Pople 6-31G**
basis set\(^{27,28}\) on all atoms, except for Ga atoms that were described with the Stuttgart effective
core potential (ECP; 28 core electrons subsumed into the potential) and valence double-zeta
basis set for the three remaining valence electrons.\(^{29,30}\) Single point energy calculations were
performed on the optimized geometries using the aug-cc-pVDZ basis set\(^{31}\) for all atoms, again
except for Ga atoms that were described with the same ECP and valence basis set used for the
geometry optimization. These calculations were carried out with both the PBE and the B3LYP XC functionals to test the effect of the physical model of the surface (given that the PBE XC functional was employed in the periodic calculations) and the XC functional. In all calculations, we applied Grimme’s semi-empirical D2 dispersion corrections\textsuperscript{21} (included to more accurately capture interactions involving adsorbates). We accounted for solvation effects using the continuum Solvation Model based on solute electron Density (SMD)\textsuperscript{32} in all geometry optimizations. Single point energy calculations with the B3LYP XC functional were performed both with and without continuum solvation to test the effect of the latter.\textsuperscript{24–26} SMD was selected because it allows efficient calculation of reaction free energies in solution, which are necessary for the computation of thermodynamic properties such as acidity constants, reduction potentials, and hydricities. While we will only compute such properties in the next chapters, we wanted to be consistent with our computational approach across this entire work and thus employed SMD in this chapter. Furthermore, it is important that this study is conducted with the same computational approach, including the same implicit solvation model, given that it also serves as a validation of the solvated cluster model that will be employed throughout this thesis. We ensured that all the identified structures were local-minimum-energy structures by calculating frequencies at the same level of theory used for geometry optimization to verify that none had imaginary frequencies. Thermal corrections at room temperature (298.15 K) were computed using the ideal gas, rigid rotor, and harmonic oscillator approximations. For all calculations involving the GaP cluster, we neglected rotational and translational contributions to the free energy since the cluster was used to simulate a crystal surface for which we would only have vibrational contributions.
Our cluster model contains 24 Ga atoms, 24 P atoms, and 40 H atoms (Figure 4.1). The H atoms were added to retain overall zero spin and to passivate the dangling bonds at the edge of the cluster that otherwise would have been bonded to other atoms in the actual material. The parts of the cluster surface that are terminated with H atoms are not reactive, and the presence of these atoms does not affect the electron density distribution in the cluster model. As a test of the model’s robustness, we demonstrate that the cluster model correctly describes the electron density distribution in the GaP(110) surface when extra electrons are added to it. For example, the relaxed geometry of the cluster model with an adsorbed hydrogen atom is very similar to the relaxed geometry of the corresponding periodic slab model with an adsorbed hydrogen atom (Figure 4.2). In both cases, the electron and the proton separate, resulting in one Ga surface atom (indicated by the red circle in Figure 4.2) rising up to adopt an sp³ configuration, as expected since it is hosting the extra electron, while the proton adsorbs on a surface P atom’s lone pair. We see the distribution of the extra electron is the same both in the cluster model and in the periodic slab, thus confirming the validity of the former. This is a crucial point to demonstrate because in this and the subsequent chapters we add extra electrons to the cluster to simulate a negatively charged photocathode.
Figure 4.2 (a) Periodic slab model and (b) cluster model of the GaP(110) surface with an adsorbed hydrogen atom on the surface. Ga atoms are represented in blue, P atoms in green, and H atoms in off-white. The red circle indicates the Ga atom where the electron from the hydrogen atom localizes. Figure adapted from Ref. 33. Copyright 2016 Royal Society of Chemistry.

The cluster model was constructed following the same procedure described in previous work.11 The initial geometry of the bare cluster in that work was cleaved from a bare periodic slab obtained from the bulk crystal relaxed without dispersion correction. In the present work, we started from the geometry of a bulk crystal relaxed with dispersion correction, in order to be consistent with the use of this correction in our adsorbate-cluster calculations.

Adsorption free energies were computed using the following equation:

$$G_{\text{ads}}(x) = G_{\text{cluster} + x} - G_{\text{cluster}} - G_x$$

(4.2)

where $G_{\text{ads}}(x)$ is the adsorption free energy of species $x$, $G_{\text{cluster} + x}$ is the free energy of the solvated GaP cluster-species $x$ complex, $G_{\text{cluster}}$ is the free energy of the solvated bare GaP cluster, and $G_x$ is the free energy of an isolated solvated $x$ molecule. Negative values of $G_{\text{ads}}(x)$ indicate thermodynamically favorable adsorption, while positive values indicate adsorption is unfavorable. We computed adsorption energies using both implicit solvation (i.e., SMD) and a mixed implicit-explicit solvation approach. We also investigated the effect of electrode negative
charge on the adsorption energies by adding extra electrons to the cluster model. For the mixed solvation approach, we used SMD in the presence of a full monolayer of half-dissociated water molecules. This was identified as the most stable water configuration at the GaP(110)/water interface in our study reported in Chapter 3 and Ref. 34. The latter was modeled by adsorbing two H$_2$O-OH$^-$ complexes, three undissociated H$_2$O molecules, and a quarter of a monolayer of protons (i.e., two adsorbed protons). This choice is explained in the next paragraph and the resulting structure is illustrated in Figure 4.3.

![Figure 4.3](image)

**Figure 4.3** (a) Top and (b) side views of the GaP(110) cluster model explicitly solvated with a full monolayer of half-dissociated water molecules. Figure adapted from Ref. 33. Copyright 2016 Royal Society of Chemistry.

To model a full monolayer of half-dissociated water molecules, we were able to add only three H$_2$O molecules in addition to 2 H$_2$O-OH$^-$ complexes along with the two proton counterions because of the geometry of the cluster model. This cluster model has eight Ga surface sites (i.e., sites available for OH$^-$ and H$_2$O adsorption) distributed over four Ga rows. The two rows at the cluster edges have one Ga site each and thus can host only one adsorbed H$_2$O molecule each. We did not place OH$^-$ on those Ga sites because, as discussed in Chapter 3 and Ref. 34, in order for
OH\(^-\) to be stable on the GaP(110) surface, an adsorbed H\(_2\)O molecule has to be hydrogen-bonded to it. Furthermore, as seen in Figure 4.3, we placed an adsorbed H\(_2\)O molecule only on one of the Ga rows at the edge of the cluster, specifically the row in which the adsorbed H\(_2\)O molecule is able to hydrogen-bond to two P sites. When we tried to place an adsorbed H\(_2\)O molecule in multiple orientations on the other Ga row at the cluster edge, multiple imaginary frequencies arise associated with rotation of the molecules along the surface plane. This indicates that hydrogen-bonding between the water protons and the P sites is needed to determine the orientation of the adsorbed H\(_2\)O molecule along the surface plane and thus reach a minimum energy structure. The two rows in the middle of the cluster each have three Ga sites. Thus, we placed one H\(_2\)O-OH\(^-\) complex (which occupies two neighboring Ga sites) and one H\(_2\)O molecule on each row. We chose to place an adsorbed H\(_2\)O molecule rather than an adsorbed OH\(^-\) because, as we just discussed, in order for OH\(^-\) to be stable, another hydrogen-bonded, adsorbed H\(_2\)O molecule would be required.

To simulate adsorption on the explicitly solvated surface, we removed adsorbed H\(_2\)O, OH\(^-\) and protons as needed to free the adsorption site for the species under study. Note that whenever we had to remove either an adsorbed OH\(^-\) or an adsorbed proton we removed also the adsorbed proton or the adsorbed OH\(^-\) next to it to always remove an overall neutral species.

**4.3 Interaction of H\(_2\)O with the GaP(110) Surface**

In the experimental setup of Bocarsly and co-workers, the GaP electrode is immersed in an aqueous solution\(^3\) charactering the interaction between the GaP(110) surface and H\(_2\)O therefore is very important. Chapter 3 presented an extensive characterization of the GaP(110)/H\(_2\)O interface, where we considered several possible adsorption configurations for water on a periodic
slab model of this surface and identified the most stable one. Here, we focus on studying the adsorption geometry and energy of an isolated, undissociated H$_2$O molecule with the main purpose of comparing the solvated cluster model results to the periodic slab model results.

Figure 4.4 (a) Side and (b) top views of H$_2$O adsorbing on the cluster model of the GaP(110) surface. Dashed black lines indicate interatomic distances predicted by the solvated cluster model (values in blue) and the periodic slab model (values in red). Ga atoms are represented in blue, P atoms in green, O atoms in red, and H atoms in off-white.

Figure 4.4 shows the adsorption geometry of an undissociated H$_2$O molecule on the GaP(110) solvated cluster model. This molecule binds to the surface via a dative bond between the H$_2$O oxygen atom and a Ga surface atom (Figure 4.4a). Furthermore, both hydrogen atoms of the H$_2$O molecule interact with the lone pairs of two nearby P surface atoms (Figure 4.4b). The same adsorption geometry was confirmed on the periodic slab model with only small variations in the Ga-O and P-H interatomic distances (0.04 Å at most).
Table 4.1 Adsorption energies of different adsorbates (H$_2$O, CO$_2$, pyridine (Py), pyridinium (PyH$^+$), and 1,2-(ortho)-dihydropyridine (o-DHP)) computed using the periodic slab + vacuum model of the GaP(110) surface with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional, the cluster model with both the PBE and the B3LYP XC functionals, and the solvated cluster model with the B3LYP XC functional. The gas phase cluster model data were obtained via single point energy calculations on the geometries optimized in the presence of the Solvation Model based on solute electron Density (SMD).

The computed adsorption energies are reported in Table 4.1 and Table 4.2, where they are compared to the adsorption energies of other molecules investigated in this chapter. Table 4.1 compares adsorption energies (without ZPE or thermal corrections) calculated with the periodic slab and cluster models using the PBE XC functional, and with the cluster model using the B3LYP XC functional in the presence and absence of continuum solvation. We can establish the effect of the physical model of the surface (second column versus third column), XC functional (third column versus fourth column), and continuum solvation (fourth column versus fifth column) on the adsorption energy by comparing the data in Table 4.1. These effects on the

<table>
<thead>
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<th>Species</th>
<th>Periodic slab + vacuum model PBE XC</th>
<th>Gas phase cluster model PBE XC</th>
<th>Gas phase cluster model B3LYP XC</th>
<th>Solvated cluster model B3LYP XC</th>
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<td>-15.3</td>
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<tr>
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<td>-8.2</td>
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<td>-28.1</td>
<td>-27.4</td>
<td>-24.5</td>
</tr>
</tbody>
</table>
overall adsorption energy trend are discussed in section 4.9. Table 4.2 reports adsorption free energies at room temperature (298.15 K) calculated with the solvated cluster model and the periodic slab model of the surface.

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption free energy (kcal/mol) at 298.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solvated cluster model</td>
</tr>
<tr>
<td>H$_2$O</td>
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</tr>
<tr>
<td>$o$-DHP</td>
<td>-8.2</td>
</tr>
</tbody>
</table>

Table 4.2 Adsorption free energies of different adsorbates (H$_2$O, CO$_2$, pyridine (Py), pyridinium (PyH$^+$), and 1,2-(ortho)-dihydropyridine ($o$-DHP)) computed using both the cluster model with implicit solvation and the periodic slab + vacuum model of the GaP(110) surface and including thermal corrections at room temperature (298.15 K).

The periodic slab model predicts an adsorption energy (-23.9 kcal/mol) larger than the cluster model (-17.2 kcal/mol) by ~7 kcal/mol. This finding is consistent with the shorter Ga-O and P-H interatomic distances predicted by the periodic slab model, and suggests that the finite cluster engenders a structural error of ~7 kcal/mol. The adsorption energy predicted by the cluster model becomes only slightly smaller (-15.3 kcal/mol) when the B3LYP XC functional is used instead of the PBE XC functional, indicating that the binding energy is already captured quite well by the non-hybrid PBE functional. Also the introduction of continuum solvation only slightly lowers the adsorption energy (-14.7 kcal/mol), suggesting that for neutral molecules
neglecting solvation effects in periodic slab calculations does not cause large errors. However, adding ZPE and thermal corrections at room temperature makes H\textsubscript{2}O much less strongly bound to the surface with both surface models (Table 4.2). Overall, we find that the adsorption free energy predicted by the periodic slab model (-9.4 kcal/mol) is larger than the adsorption free energy predicted by the solvated cluster model (-2.0 kcal/mol), as expected based on the analysis presented above and the data in Table 4.1, which attributes the binding free energy differences largely to structural model differences. The actual adsorption free energy will likely lie in between the values predicted by the periodic slab and solvated cluster models, with a best estimate of \(-9.4 + 2.5 = -6.9\) kcal/mol (based on corrections for functional and solvation errors determined with cluster model calculations). Based on the computed adsorption free energies, we conclude that an undissociated H\textsubscript{2}O molecule favorably binds to the GaP(110) surface at room temperature (298.15 K).

4.4 Interaction of CO\textsubscript{2} with the GaP(110) Surface

CO\textsubscript{2} is the species being reduced in the experimental system,\textsuperscript{3} so our aim is to understand its reduction mechanism. A crucial point is to figure out whether or not it favorably interacts with the electrode surface. We found that CO\textsubscript{2} most favorably adsorbs on GaP(110) with a linear and tilted adsorption geometry, as shown in Figure 4.5. In this geometry, one CO\textsubscript{2} oxygen atom interacts weakly with a Ga surface site (Figure 4.5a). The Ga-O interatomic distance predicted by the periodic slab model is shorter (2.62 Å) than the distance predicted by the solvated cluster model (2.80 Å).

The periodic slab model predicts a slightly larger adsorption energy (-6.6 kcal/mol) than the cluster model (-6.2 kcal/mol) when using the PBE XC functional, which is consistent with
the difference in Ga-O interatomic distance and the very weak interaction between CO\textsubscript{2} and GaP that is not very sensitive to the structural model. The small CO\textsubscript{2} adsorption free energy is also consistent with the long interatomic distances (3.36 Å and 3.44 Å predicted by the cluster and periodic slab models, respectively) between the electron-poor CO\textsubscript{2} carbon atom and the lone pairs on two nearby surface P atoms (Figure 4.5b).

![Figure 4.5](image)

Figure 4.5 (a) Side and (b) top views of CO\textsubscript{2} adsorbing on the cluster model of the GaP(110) surface. Dashed black lines indicate interatomic distances predicted by the solvated cluster model (values in blue) and the periodic slab model (values in red). Ga atoms are represented in blue, P atoms in green, O atoms in red, C atoms in purple, and H atoms in off-white.

The PBE and the B3LYP XC functionals predict the same adsorption energy (-6.2 kcal/mol), again illustrating that the PBE functional used in the slab calculation is adequate. The introduction of continuum solvation (which changes the binding energy to be only slightly less negative) as well as ZPE and thermal corrections (-0.7 kcal/mol adsorption free energy predicted by the periodic slab model and +2.5 kcal/mol predicted by the solvated cluster model) cause the adsorption energy to become smaller, as we have already observed for H\textsubscript{2}O. The CO\textsubscript{2} adsorption free energy is smaller than the H\textsubscript{2}O adsorption free energy, consistent with the longer Ga-O
interatomic distance predicted for CO₂ and as expected based on the relative Lewis basicity of the two molecules. The weaker interaction between CO₂ and the surface explains the larger variation in Ga-O interatomic distance found with the two models (0.18 Å difference between the periodic and cluster models) in comparison to H₂O (0.02 Å difference).

Overall, we expect the actual adsorption free energy for CO₂ to lie in between the values computed with the periodic slab and solvated cluster models, with a best estimate of -0.7 + 1.0 = +0.3 kcal/mol, (based on corrections for functional and solvation errors). The low adsorption free energy confirmed by both models suggests that CO₂ does not chemisorb but at most physisorbs on the GaP(110) surface. The strength of this interaction is too weak for CO₂ adsorption to be favored at room temperature, especially when in competition with other species present in solution.

4.5 Interaction of Pyridine with the GaP(110) Surface

CO₂ reduction at underpotentials has only been observed when Py is added to the aqueous solution in contact with the electrode. Furthermore, in the experimental system using GaP electrodes, the solution pH (5.2) is almost equal to the PyH⁺ pKₐ (5.3) so that about half of the Py molecules will remain deprotonated. These experimental details suggest that the active catalyst in this system is likely to be either Py itself or a species derived from it. Thus, characterizing the interaction between Py and the electrode surface represents a crucial step towards understanding the catalytic mechanism in this system and the catalytic role played by Py. Here, we first calculate the Py adsorption geometry and energy using both our cluster and periodic slab models of the surface as we did for the other species discussed in this chapter. Next, we present the results of a more in-depth investigation of Py interaction with GaP(110),
conducted in collaboration with the experimental group of Professor Bruce E. Koel at Princeton University.\textsuperscript{12}

4.5.1 Adsorption Geometry and Energy of Pyridine on GaP(110)

The preferred adsorption geometry of Py on GaP(110) was first identified by Professor Ana B. Muñoz-García, a former postdoctoral research associate in our group, from a series of configurations of adsorbed Py generated by varying a selected dihedral angle able to describe the rotation of Py around the N-Ga bond formed with the surface. Upon relaxation of these configurations, she found that the most stable adsorption geometry of Py on GaP(110) consists of the Py molecule tilted away from the surface, as shown in Figure 4.6. In this adsorption geometry, Py favorably adsorbs on the GaP(110) surface at room temperature with an adsorption energy of -32.2 kcal/mol and -27.8 kcal/mol predicted by the periodic slab and cluster models with the PBE XC functional, respectively; here the difference in structural models gives rise to a difference in binding energies intermediate between H$_2$O and CO$_2$. As seen for H$_2$O, the B3LYP functional predicts an only slightly lower adsorption energy (-26.2 kcal/mol) compared to PBE and adding solvation energy corrections makes the adsorption energy even less negative (-23.6 kcal/mol). Here the deviations between periodic slab + vacuum and solvated cluster models are more evenly split between structural and solvation/functional changes. Consistent with the adsorption energy trend, the periodic slab model predicts a shorter Ga-N interatomic distance (2.12 Å) than the solvated cluster model (2.15 Å) (Figure 4.6a). Adding ZPE and thermal corrections causes the adsorption energy at room temperature to become less negative but adsorption is still favorable, as predicted by both the periodic slab model (-16.7 kcal/mol) and the solvated cluster model (-9.3 kcal/mol), with the expectation that the actual binding energy
lies in between (best estimate is \(-16.7 + 4.2 = -12.5\) kcal/mol, based on corrections for functional and solvation errors).

Figure 4.6 (a) Side and (b) top views of pyridine (Py) adsorbing on the cluster model of the GaP(110) surface. Dashed black lines indicate interatomic distances predicted by the solvated cluster model (values in blue) and the periodic slab model (values in red). Ga atoms are represented in blue, P atoms in green, N atoms in light blue, C atoms in purple, and H atoms in off-white.

The electron density difference plots (Figure 4.7) show that there is a shift of electrons from the site of the N lone pair toward the Ga atom, a feature that is characteristic of a dative bond. This observation is confirmed by the computed Bader charges\(^{35,36}\) for the adsorbed Py (q = +0.11) and the slab (q = -0.11) indicating a net transfer of electrons from the molecule to the surface.
4.5.2 Reactivity of Adsorbed Pyridine from Simulated and Experimental Scanning Tunneling Microscope Images

Our experimental collaborators performed measurements of the GaP(110) surface exposed to Py using a scanning tunneling microscope (STM). We used the computed partial electron density to interpret their observations.\textsuperscript{12} First, we validated our computational approach by demonstrating that our simulated STM images based on the computed partial electron density are in good agreement with experimental STM images. Then, we used isosurfaces of electron density derived from the computed partial electron density to qualitatively characterize the states of adsorbed Py, which were sampled by applying different biases in the STM experiments. This combined experimental and theoretical study brings new insights into adsorbed Py reactivity and its implications for catalytic CO\textsubscript{2} reduction on GaP electrodes.
4.5.2.1 Scanning Tunneling Microscope Image Simulation**

The STM image simulation was performed based on the theory developed by J. Tersoff and D. R. Hamann.\textsuperscript{37} This theory establishes a dependence of the current on the resulting local density of states (LDOS) from a given applied voltage. We used VASP to compute the partial electron density in a specific energy range (\textit{i.e.}, the LDOS) determined by the applied voltage in the experiments. Furthermore, the calculation of the current using the Tersoff-Hamann approximation also requires the tip work function and the tip radius. We approximated these parameters as 4.55 eV and 3 bohr, respectively. They correspond to the work function\textsuperscript{38} and roughly the metallic radius (\textasciitilde2.6 bohr)\textsuperscript{39} of body-centered cubic tungsten, which was the tip used in the experiment. Using the metallic radius as the radius of the tip is a valid approximation because the electron tunneling between the sample and the tip will be primarily from the outermost atom of the tip into the sample or \textit{vice versa}. Based on the computed partial electron density and these parameters, we computed the tunneling current at different points in space and used these results to simulate two-dimensional STM images in both constant current and constant tip height modes. Constant current images were obtained by plotting the tip height for which the current is equal to the chosen constant value as a function of the position of the tip in the \textit{xy} plane (\textit{i.e.}, the plane of the surface). On the other hand, constant height images were obtained by plotting the current, at a given tip height, as a function of the position of the tip in the \textit{xy} plane.

Finally, we computed isosurfaces of electron density by integrating over specific energy ranges near the Fermi energy ($E_F$) corresponding to the energy ranges probed by STM.

\textsuperscript{**} The simulation of the scanning tunneling microscope images was performed using a code developed by Dr. John Mark P. Martirez, who is currently a postdoctoral research associate in our group.
Isosurfaces integrated over different ranges were normalized according to the number of bands included in the sampled energy range. The isosurface levels used for the electron density plots were 0.01650 e/bohr$^3$ for the -3.00 eV to $E_F$ energy range, 0.0006 e/bohr$^3$ for the $E_F$ to 0.60 eV energy range, and 0.00225 e/bohr$^3$ for the $E_F$ to 3.00 eV energy range.

4.5.2.2 Results

Our simulated STM images are in good agreement with the experimental STM images. Figure 4.8a shows an experimental constant-current STM image at 2.35 V and Figure 4.8b shows a simulated STM image at the same length scale for comparison. All major features of the experimental image are reproduced by the simulation. The constant-height STM images are also in excellent agreement, where the computed STM image (Figure 4.8d) correctly reproduces the double lobed structure observed in the experiments (Figure 4.8c). This comparison also allows us to correctly assign the molecule’s orientation on the surface in the STM experiments: the bigger lobe corresponds to the N-Ga bond, whereas the smaller lobe corresponds to the rest of the Py ring.

Overall, based on the comparison between experimental and simulated STM images, we concluded that the partial electron density generated by the DFT calculations comprehensively describes the electronic structure of the experimental model system and can be used directly to interpret the experimental results. Specifically, given the correspondence between experimental and simulated images, it is possible to further interpret the system qualitatively through isosurfaces of electron densities in the same energy ranges close to the $E_F$ probed by STM.
Figure 4.8 Comparison between experimental and simulated scanning tunneling microscope (STM) images of pyridine (Py)/GaP(110). (a) Constant-current STM image at 5 K. Tunneling parameters: 2.35 V, 0.04 nA, 15×15 Å. To suppress noise the STM image has been smoothed by a Gaussian with a 2 pixel radius. (b) Simulated constant-current STM image based on the density functional theory (DFT)-relaxed adsorption geometry of Py on GaP(110) shown at the same length scale as the STM image in (a). (c) Constant-height STM image. The color scale is linear and the image reflects tunneling currents from 0 nA to about 1 nA. Other tunneling parameters: 2.4 V, 13.9×13.9 Å. (d) Simulated constant-height STM image at the same length scale as the STM image in (c). (e) Illustration of Py orientation in the experimental and simulated images in (a), (b), (c), and (d). Figure adapted from Ref. 12. Copyright 2015 American Chemical Society.

Our collaborators probed different occupied and unoccupied states of the sample by varying the applied sample bias in their STM experiments. Occupied states (e.g., lone pairs on surface P atoms) were probed when applying a negative bias below $E_F$. Unoccupied states (e.g., the empty orbitals of the surface Ga atoms) were probed when applying a positive bias above $E_F$. 

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Isosurfaces of electron density generated from the DFT partial electron density can be used to visualize the occupied and unoccupied states of adsorbed Py probed in the STM experiments and hence gain insights into its reactivity. We use the isosurfaces here to further understand the spatial organization of occupied and unoccupied states within the Py-GaP surface complex, as has been done previously in the literature on other systems.\textsuperscript{40} Adjacent to the corresponding constant-height STM images, Figure 4.9 shows three perspectives of the isosurfaces of electron density when integrated over the energy ranges corresponding to those probed by experiment.

Figure 4.9 Isosurfaces of electron density plotted for three energy ranges: Fermi energy ($E_F$) to conduction band minimum (CBM) + 1.0 eV (top), $E_F$ to CBM + 0.6 eV (middle), and valence band minimum (VBM) - 3.0 eV to $E_F$ (bottom). The electron density associated with the GaP slab is not displayed so that the electron density associated with the adsorbed pyridine (Py) molecule is more visible. Corresponding constant-height scanning tunneling microscope (STM) images shown at left.
Figure 4.10 Combined experimental and density functional theory (DFT) results showing that by spatially resolving the lowest unoccupied molecular orbital (LUMO), the scanning tunneling microscope (STM) images predict the sites susceptible to nucleophilic attack (labelled as \( \text{Nu}^- \) in the figure) on adsorbed pyridine (Py) by hydrides (or hydride equivalents, \textit{vide infra}), along with protons from solution to produce 1,2-(ortho)-dihydropyridine (\( o \)-DHP) or 1,4-(para)-dihydropyridine (\( p \)-DHP), as described in Refs. 4,5. Figure adapted from Ref. 12. Copyright 2015 American Chemical Society.

The lowest unoccupied molecular orbital (LUMO) states, represented by the density integrated from \( E_F \) to 0.6 above the conduction band minimum (CBM), clearly show the differentiation of orbital lobes probed by experiment in this energy range. The visualization of these LUMO states allow us to draw important conclusions on the mechanism previously proposed by Keith and Carter\(^4,5\) and more generally on the reactivity of adsorbed Py towards nucleophilic attack. In the proposed mechanism, adsorbed Py works as a hydride shuttle to CO\(_2\) and thus must first react with a nucleophilic hydrogen, such as a surface hydride. Keith and Carter\(^4,5\) have noted the most chemically intuitive carbon sites for nucleophilic attack on adsorbed Py by adsorbed hydride are C2, C4, and C6. Figure 4.9 and Figure 4.10 indicate that
these sites largely contribute to the LUMO states. Therefore, we conclude that the experimental
STM images support the mechanism proposed by Keith and Carter, where Py undergoes
nucleophilic attack on either the C2/C6 site or the C4 site by a surface hydride or other hydride
equivalent (vide infra) resulting in either 1,2-(ortho)-dihydropyridine (o-DHP) or 1,4-(para)-
dihydropyridine (p-DHP) formation, respectively.4, 5

4.6 Interaction of Pyridinium with the GaP(110) Surface

The pH of the aqueous solution used in the experiments (5.2) is nearly equal to the pKₐ of PyH⁺
(5.3).3 About half of the Py molecules will be protonated to form PyH⁺ under these conditions.
Furthermore, in previous experimental work, no reduction was observed when the pH was larger
than 7.6 Overall, these experimental observations suggest that the acidic pH and possibly PyH⁺
are essential for CO₂ reduction. Therefore, it is important to study how PyH⁺ interacts with the
electrode surface. As previously noted in section 4.2.1, only cluster calculations were employed
for this investigation because periodic calculations would have required the use of an unphysical
uniform background charge to neutralize the positive charge of PyH⁺.

We found that PyH⁺ mainly interacts with the surface via electrostatic attraction between
the proton bound to PyH⁺ nitrogen atom and the lone pairs belonging to two P surface sites
(Figure 4.11b). PyH⁺ is not able to interact with the surface via a N-Ga dative bond like Py does,
because the N lone pair is already binding to a proton. In fact, the Ga-N interatomic distance for
PyH⁺ (Figure 4.11a) is more than 1 Å larger than the same distance predicted for adsorbed Py.
The adsorption energy of PyH⁺ is very negative, as predicted by both the PBE (-42.0 kcal/mol)
and the B3LYP XC functionals (-40.5 kcal/mol). However, the inclusion of solvation causes a
drastic change in adsorption energy, which becomes much smaller (-8.2 kcal/mol). Thus PyH⁺ is
significantly stabilized in the homogeneous phase by solvation effects, as we already concluded in our previous work.\textsuperscript{11} Finally, the inclusion of ZPE and thermal corrections yields a positive adsorption free energy (+5.5 kcal/mol), thus suggesting that PyH\textsuperscript{+} adsorption is not favorable at room temperature. We therefore conclude that, if involved in the catalytic mechanism, PyH\textsuperscript{+} will operate in solution rather than being adsorbed on the surface. On the other hand, here we neglected the fact that the GaP electrode is negatively charged in the experiments,\textsuperscript{3} so a positively charged species like PyH\textsuperscript{+} might be favorably attracted to it. In section 4.8, we investigate the effect of negatively charging the surface on the adsorption free energy of PyH\textsuperscript{+} and the other species considered in this chapter.

Figure 4.11 (a) Side and (b) top views of pyridinium (PyH\textsuperscript{+}) adsorbing on the cluster model of the GaP(110) surface. Dashed black lines indicate interatomic distances predicted by the solvated cluster model (values in blue). Ga atoms are represented in blue, P atoms in green, N atoms in light blue, C atoms in purple, and H atoms in off-white.

### 4.7 Interaction of Dihydropyridine with the GaP(110) Surface

Adsorbed DHP was proposed as the active catalyst in the heterogeneous mechanism of CO\textsubscript{2} reduction on GaP electrodes, and it was found that the reduction of Py to DHP both in solution
and on the surface has a moderate reduction potential. Identifying DHP’s most favorable adsorption geometry, as well as studying the strength of the interaction between DHP and the GaP(110) surface, thus are necessary steps for the study of this proposed mechanism. Note that two possible isomers of DHP could form: \( o \)-DHP and \( p \)-DHP. In this thesis work, we consider only \( o \)-DHP. This choice simplifies the discussion without undermining our conclusions, since previous work demonstrated that the two isomers have similar adsorption energies and reduction potentials. Furthermore, \( o \)-DHP is likely more easily formed if its formation occurs via surface hydride transfer to Py, given that the Py carbon atom undergoing nucleophilic attack is closer to the proposed active surface hydride.

Figure 4.12 (a) Side and (b) top views of 1,2-(ortho)-dihydropyridine (\( o \)-DHP) adsorbing on the cluster model of the GaP(110) surface. Dashed black lines indicate interatomic distances predicted by the solvated cluster model (values in blue) and the periodic slab model (values in red). Ga atoms are represented in blue, P atoms in green, N atoms in light blue, C atoms in purple, and H atoms in off-white.

\( o \)-DHP adsorbs in a similar fashion to Py, via a dative bond from N to a surface Ga. Thus, we performed a similar search for the preferred adsorption configuration as the one previously
performed for Py. We generated a series of configurations by varying a selected dihedral angle able to describe the rotation of o-DHP around the N-Ga bond formed with the surface. We then relaxed these configurations and identified the most favorable adsorption geometry as shown in Figure 4.12. The periodic slab model predicts a slightly stronger interaction between o-DHP and the GaP(110) surface (-30.7 kcal/mol adsorption energy) than the cluster model (-28.1 kcal/mol). In contrast, the Ga-N interatomic distance (Figure 4.12a) calculated with the periodic slab model is slightly longer (0.02 Å) than the distance calculated with the cluster model. On the other hand, while one of the two relevant P-H interatomic distances (Figure 4.12b) is predicted to be almost the same by the two models (0.01 Å difference), the periodic slab model predicts the other P-H distance to be 0.06 Å shorter than the cluster model. This shorter P-H distance may explain the stronger o-DHP/GaP(110) interaction predicted by the periodic slab model. Once again, the B3LYP XC functional predicts a slightly smaller adsorption energy (-27.4 kcal/mol) than the PBE XC functional (-28.1 kcal/mol) and the adsorption energy becomes even less negative when solvation effects (-24.5 kcal/mol) and thermal corrections are accounted for. The solvated cluster model (-8.2 kcal/mol adsorption free energy) and the periodic slab model (-12.9 kcal/mol) both predict that o-DHP will adsorb at room temperature, with a best estimate for the actual adsorption energy being -9.3 kcal/mol (3.6 kcal/mol corrections for functional and solvation errors). Note that the smaller adsorption free energy and the longer measured interatomic Ga-N distance (predicted by both models) in comparison to Py suggests that o-DHP interacts less strongly with GaP(110). This observation is explained by the fact that o-DHP is a bulkier molecule than Py and thus has more steric repulsion with the surface.
4.8 Explicit Solvation and Surface Negative Charge Effects on Computed Adsorption Energies

We now use our cluster model to investigate the effect of explicit solvation of the surface and negatively charging the surface. The former effect is important because the surface is exposed to water in the experimental system,\(^3\) and we have previously found (Chapter 3 and Ref. 34) that a full monolayer of half-dissociated water molecules adsorbs on the GaP(110) surface under these conditions. The latter effect is important because a negative bias is applied to the GaP electrode under experimental conditions.\(^3\) The explicit water monolayer adsorbed on the cluster model and the surface negative charge were modeled as described in section 4.2.2.

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption free energy (kcal/mol) at 298.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Implicit solvation</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>-2.0</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>+2.5</td>
</tr>
<tr>
<td>Py</td>
<td>-9.3</td>
</tr>
<tr>
<td>PyH(^+)</td>
<td>+5.5</td>
</tr>
<tr>
<td>o-DHP</td>
<td>-8.2</td>
</tr>
</tbody>
</table>

Table 4.3 Adsorption free energies of relevant species (H\(_2\)O, CO\(_2\), pyridine (Py), pyridinium (PyH\(^+\)), and 1,2-(ortho)-dihydropyridine (o-DHP)) on the solvated GaP cluster model at 298.15 K computed using both the implicit and mixed implicit-explicit solvation schemes.

Table 4.3 compares the adsorption free energies computed with both the implicit and mixed implicit-explicit solvation approaches. Overall, we find that the implicit solvation approach largely gives the same adsorption free energy trend as the more accurate mixed
solvation approach. The presence of the explicit water layer on the surface causes all of the adsorption free energies, except for o-DHP, to become smaller with a maximum increase of 3.1 kcal/mol in the case of PyH⁺. One possible explanation for the larger adsorption free energy calculated for o-DHP is that its molecular structure and adsorption geometry allow it to interact more strongly with the co-adsorbed explicit water molecules than the other species under investigation do. Based on the overall agreement between the two solvation schemes, we decided to use only the implicit solvation scheme to study the effect of the electrode negative charge. The results of this study are summarized in Table 4.4.

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption free energy (kcal/mol) at 298.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface charge=0</td>
</tr>
<tr>
<td>H₂O</td>
<td>-2.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>+2.5</td>
</tr>
<tr>
<td>Py</td>
<td>-9.3</td>
</tr>
<tr>
<td>PyH⁺</td>
<td>+5.5</td>
</tr>
<tr>
<td>o-DHP</td>
<td>-8.2</td>
</tr>
</tbody>
</table>

Table 4.4 Adsorption free energies of relevant species (H₂O, CO₂, pyridine (Py), pyridinium (PyH⁺), and 1,2-(ortho)-dihydropyridine (o-DHP)) on the neutral and negatively charged implicitly solvated GaP cluster model at 298.15 K. Surface charges -1 e and -2 e were simulated by adding one and two extra electrons to the system, respectively; these correspond to approximate surface charge densities of 0.010e / Å² and 0.020e / Å², respectively, based on the surface area of the cluster model used (96 Å²).
We found that the adsorption free energy trend obtained with the implicitly solvated neutral cluster model is preserved when the electrode negative charge is simulated (via addition of extra electrons to the cluster to model). In the case of PyH⁺, the change is more pronounced (2 kcal/mol decrease upon addition of two extra electrons), which is explained by electrostatic attraction between PyH⁺ and the negatively charged cluster. Overall, these studies confirm that the results found with the implicitly solvated, neutral cluster model are robust: only H₂O, Py, and o-DHP favorably interact with the electrode surface, while for CO₂ and PyH⁺ this interaction is not favorable. The implications of these results for the CO₂ reduction mechanism are discussed in the next section.

4.9 Discussion

The periodic slab and cluster models of the GaP(110) surface predict the same adsorption free energy trend (see Table 4.2 for a summary and comparison). The adsorption free energy differences between the two models are explained based on the different XC functional and solvation choices, as mentioned already above. The relevant interatomic distances are in reasonable agreement, and their differences are consistent with the adsorption free energy variation between the two models. We therefore conclude that our cluster model can be trusted to model the GaP(110) periodic surface.

In general, the periodic slab model predicts higher adsorption free energies compared to the neutral, solvated cluster model (see Table 4.2 for comparison). The adsorption energy data reported in Table 4.1 demonstrates that two differences between the models are responsible for this observation (beyond the fact that they are different physical models of the surface): 1) the use of different XC functionals (PBE in the periodic calculations and B3LYP in the cluster
calculations), and 2) the use of an implicit solvation model in the cluster calculations. In agreement with our previous work,\textsuperscript{11} we found that the PBE XC functional predicts higher binding energies than the hybrid B3LYP XC functional. The different XC functional employed in the two types of calculations thus helps explain the higher binding energies predicted with the periodic slab model. Only in the case of CO\textsubscript{2} did we not observe any XC functional effect, which can be explained by the very weak interaction between this molecule and the surface. The isolated molecule in the homogeneous (gas or solution) phase (i.e., the reference state for the calculation of the adsorption free energy according to Eqs. (4.1) and (4.2)) is likely more stabilized in the cluster calculations because of the simulated solvation effects, which are absent in the periodic slab calculations conducted in vacuum. This leads to the weaker adsorption strengths predicted by the cluster model. This effect was particularly significant for PyH\textsuperscript{+}, which is greatly stabilized in the solution phase because of its positive charge.

The same adsorption free energy trend identified with the neutral, implicitly solvated cluster model and the periodic slab model of the GaP(110) surface was also found to hold when using the cluster model to simulate relevant experimental conditions (i.e., water adsorption on the photocathode surface and photocathode negative charge).\textsuperscript{3} Therefore, we can now use these results to gain some relevant mechanistic insights. The positive adsorption free energy predicted for CO\textsubscript{2} suggests that CO\textsubscript{2} cannot be directly reduced at the surface, especially given that other species, such as H\textsubscript{2}O, Py, and DHP, favorably adsorb on the surface. Either the surface itself or a surface-adsorbed catalyst therefore is needed to shuttle electrons to CO\textsubscript{2}. Experimental observations suggest that such a catalyst is likely derived from Py.\textsuperscript{3,6–10} PyH\textsuperscript{+} is unlikely to play this role, given that it does not favorably adsorb; in contrast, both Py and DHP favorably adsorb and are plausible candidates for this role. In the mechanism proposed by Keith and Carter,\textsuperscript{4,5}
adsorbed DHP would be the active catalyst postulated to form via surface hydride transfer to Py. The fact that both Py and DHP were found to favorably adsorb suggest that Py reduction to DHP may occur at the surface. This Py reduction pathway is also supported by the results of our combined experiment-theoretical study on the Py/GaP(110) interface, showing that adsorbed Py is reactive towards nucleophilic attack.¹²

4.10 Conclusions

In summary, we have characterized the interaction between relevant species and the electrode surface employed in the Bocarsly system for catalytic CO₂ reduction.³ There were two primary goals: to 1) gain new mechanistic insights based on the adsorption properties of these species, and 2) validate the GaP(110) surface cluster model that will be extensively used in the next chapters. We computed adsorption free energies and geometries with both this cluster model and a periodic slab model of the GaP(110) surface, finding good agreement. We then studied the effect of explicit solvation, as well as surface negative charge, and found that the same adsorption free energy trend holds true. Specifically, we found that neither CO₂ nor PyH⁺ favorably adsorbs, while Py and DHP do absorb. This finding suggests that an adsorbed Py-based catalyst is needed to shuttle electrons from the surface to CO₂. This also suggests that the catalyst can be either Py or DHP, among the Py-based species investigated so far. Keith and Carter previously proposed that adsorbed DHP is formed via surface hydride transfer to adsorbed Py and catalyzes CO₂ reduction.⁴,⁵ Their computed reduction potentials⁴,⁵¹ and our combined experimental-theoretical study¹² supported this hypothesized pathway for adsorbed DHP formation.
4.11 References


Chapter 5

Stability of Surface Protons in Pyridine-Catalyzed CO$_2$ Reduction at p-GaP Photoelectrodes††

5.1 Introduction

In Chapter 1, we discussed how preliminary insights into the catalytic mechanism of CO$_2$ reduction in the Bocarsly system can be gained from relevant experimental observations. First, the dependence of selectivity and underpotentials on the electrode material suggests that the electrode is likely involved in the mechanism.$^{1-6}$ Second, underpotentials are only observed when pyridine (Py) is added to the solution, which suggests that a Py-derived species might be an active co-catalyst in this system.$^{1-6}$ Third, reduction phenomena were only observed under acidic pH conditions, thus suggesting that protons are required for the catalysis to occur.$^1$ These observations provide constraints as we work to establish the validity of previously proposed mechanisms for CO$_2$ reduction in this system.

Overall, among the mechanisms proposed by other groups and by our group prior to this thesis work (section 1.3.2 of Chapter 1), the only mechanism that could explain these experimental observations is the heterogeneous mechanism on GaP(110) in which dihydropyridine (DHP) is the active catalyst (Figure 5.1).$^{7,8}$ None of the steps of this mechanism have been tested yet. It was previously determined that the adsorbed protons with hydride character needed for DHP production can be formed by water dissociation on GaP(110) (Chapter

†† Reproduced in part from Lessio, M.; Riplinger, C.; Carter, E. A. Phys. Chem. Chem. Phys. 2016, 18, 26434-26443 (both main text and supplementary information) with permission from the Royal Society of Chemistry.
A key question in validating the first step of the proposed mechanism is whether these species will be stable under experimental conditions. Stable adsorbed protons could then be reduced to surface hydrides and potentially react with adsorbed Py to form the active catalytic species DHP, a necessary (but not sufficient) condition for the proposed mechanism’s validity. DHP formation requires not only hydride but also proton availability, whether formation occurs concertedly (via a proton-coupled hydride transfer) or sequentially (hydride followed by proton transfer or vice versa). In the proposed mechanism for adsorbed DHP formation, the protons are provided by the aqueous solution in contact with the electrode. However, we cannot exclude a priori that protons could be transferred from the surface as well. Depending on the adsorption geometry of the molecule that has to be protonated, transfer of protons from the surface might be easier than transfer from solution. For instance, in the case of DHP, the N atom that has to be protonated is directly bound to the surface and thus may be more easily accessible to adsorbed protons. Furthermore, independent of the proposed mechanism under investigation, CO$_2$ reduction to methanol necessarily requires a proton source. Therefore, while this work focuses on the mechanism proposed by Keith and Carter,\textsuperscript{7,8} the results presented are relevant to any proposed mechanism for heterogeneous (photo)electrocatalytic CO$_2$ reduction on GaP. For instance, in the proposed homogeneous mechanism with DHP as the active catalyst (section 1.3.2 of Chapter 1),\textsuperscript{11} Poisson-Boltzmann theory was used to study the availability of protons in proximity to the surface. However, a specific proton source was not identified. In this chapter, we therefore investigate the relative stability of adsorbed protons to shed light on any role they may play.
Figure 5.1 Proposed heterogeneous mechanism for pyridine (Py)-catalyzed CO$_2$ reduction on the GaP(110) surface from Refs. 7,8. In this mechanism, dihydropyridine (DHP) is formed by reaction of adsorbed Py with adsorbed hydride-like species and protons from solution. Once formed, DHP plays the role of the active co-catalyst facilitating the transfer of protons and electrons to CO$_2$. This figure is a reproduction of Figure 1.3 from Chapter 1 and it is reproduced here for the reader’s convenience.

Using cluster models previously developed and extensively validated by our group (Chapter 4 and Ref. 12), we compute the $pK_a$ of the adsorbed protons under relevant experimental conditions and we compare them to the $pK_a$s of other species directly involved in the postulated mechanism. With these results, we are able to determine whether the adsorbed protons can form, whether they are stable against proton transfer to other species and thus whether they will be available to be reduced to surface hydrides under experimental conditions. We note that the $pK_a$ is the correct property to calculate for this purpose. The adsorbed “hydrides” that are involved in the proposed mechanism for DHP generation are formed by proton adsorption onto surface phosphorus lone pairs; the adsorbed protons develop hydride character upon adsorption. Thus, the $pK_a$ can be used to determine whether the surface “hydrides” can be formed and are stable, as their formation requires proton adsorption. Eventually, assessing the hydricity of these species will be essential to determine whether they are able to reduce adsorbed Py to adsorbed DHP; we are currently working on this aspect. The
computed $pK_a$ specifically helps us determine whether the adsorbed protons can simultaneously serve as the proton source needed for DHP formation. These $pK_a$s also can be used as a guide to assess which proton transfer processes might be feasible before proceeding to expensive evaluations of reaction barriers. Overall, such insights allow us to draw conclusions on the viability of the proposed mechanism and are relevant to the general understanding of heterogeneous (photo)electrocatalytic CO$_2$ reduction.

5.2 Computational Approach

All calculation details are the same as those reported for the cluster calculations in section 4.2.2 of Chapter 4. As discussed there, our solvation approach was determined to make the $pK_a$ computation both accurate and efficient. We again accounted for solvation effects using the continuum Solvation Model based on solute electron Density (SMD)$^{13}$ in all calculations. In this study, the continuum solvation model COnductor-like Screening MOdel (COSMO)$^{14}$ was also tested, but better agreement between computed and experimental $pK_a$s was obtained using SMD ($\textit{vide infra}$). In addition, here we used explicit water molecules where necessary ($\textit{vide infra}$).

$pK_a$s were computed from reaction free energies in solution ($\Delta G_{aq}$) using the following equation:

$$pK_a(AH^+) = -\log_{10} K_a = +\Delta G_{aq}/2.303RT \quad (5.1)$$

$\Delta G_{aq}$ is often computed using thermodynamic cycles that require calculation of the reaction free energy in the gas phase and the solvation energy for each species involved in the dissociation equilibrium. However, recent studies using SMD showed that it is possible to avoid thermodynamic cycles and save computational time by directly computing $\Delta G_{aq}$ without
incurring larger errors affecting the computed pK_a.s. Here, we tested both approaches using SMD and COSMO to determine the best method for computing pK_a.s of relevant species. The results of this study are summarized in Figure 5.2.

Figure 5.2 Effect of solvation model (COnductor-like Screening MOdel (COSMO) vs. Solvation Model based on solute electron Density (SMD)) and pK_a computational approach (thermodynamic cycle vs. direct approach) on the computed pK_a.s of relevant species in the system (H_2O, H_3O^+, 1,2-(ortho)-dihydropyridine (o-DHP), pyridinium (PyH^+), and HCOOH).

Getting the right trend of pK_a.s for pyridinium (PyH^+) and HCOOH was especially important and challenging. SMD captures the correct trend (experimental HCOOH pK_a < experimental PyH^+ pK_a) whereas COSMO does not. Furthermore, very similar results were obtained when using thermodynamic cycles and when directly computing reaction free energies in solution with both SMD and COSMO. Therefore, we used the direct approach with SMD for all results presented in this chapter. For both H_2O and H_3O^+, the computed pK_a is far from the experimental value, independent of the solvation model and the pK_a computational approach.
used. As discussed below, much better agreement with the experimental value is reached when a mixed implicit-explicit solvation approach is used.

Thus, we applied the direct approach in which $\Delta G_{aq}$ for a generic proton dissociation reaction $AH^+ \rightarrow A + H^+$ was obtained using the following equation:

$$\Delta G_{aq} = G_{aq}(A) + G_{aq}(H^+) - G_{aq}(AH^+) \quad (5.2)$$

Here $G_{aq}$ represents the free energy in solution at room temperature. We used the empirical value of -270.3 kcal/mol for $G_{aq}(H^+)$ following previous work.\textsuperscript{7,17–19} As extensively discussed in one of these studies,\textsuperscript{18} this term includes the empirical gas phase free energy of a proton (-6.3 kcal/mol), the proton solvation energy (-265.9 kcal/mol), and the energy contribution due to the standard state change from gas phase to solution phase (+1.89 kcal/mol).

For simulation of species in solution, we added explicit water molecules to improve the description of solvation effects. Specifically, we added two explicit water molecules for H$_2$O, three for H$_3$O$^+$, one for 1,2-(ortho)-dihydropyridine ($\text{o}$-DHP) and PyH$^+$, and three for HCOOH. For H$_2$O and H$_3$O$^+$, we used known solvation structures (i.e., H$_2$O trimer and H$_3$O$^+$ Eigen cation with three solvating H$_2$O molecules). For o-DHP and PyH$^+$, we added one water molecule to hydrogen bond to the hydrogen bound to the nitrogen atom. For HCOOH, we added three water molecules in total: two water molecules hydrogen-bonded to the two oxygen atoms and one water molecule hydrogen-bonded to the acidic hydrogen atom. This solvation structure was found in a previous study to give the best agreement between computed and experimental pK$_a$'s for HCOOH.\textsuperscript{20} pK$_a$'s of species in solution obtained with different numbers of solvating water molecules are summarized in Figure 5.3. Except for PyH$^+$, the pK$_a$'s are significantly improved,
especially for water and H$_3$O$^+$, by using the mixed implicit-explicit solvation scheme and hence those models are deployed in the discussion below.

Figure 5.3 Effect of varying numbers of explicit solvent (water) molecules on the pK$_a$s of relevant species (H$_2$O, H$_3$O$^+$, 1,2-(ortho)-dihydropyridine (o-DHP), pyridinium (PyH$^+$), and HCOOH) computed with the Solvation Model based on solute electron Density (SMD) and the direct approach.

5.3 Results and Discussion

In the proposed heterogeneous mechanism on GaP(110) (Figure 5.1), the active catalytic species adsorbed DHP is formed by transfer of a proton and a hydride; the hydride is an adsorbed proton with hydride character. Clearly, for this mechanism to be viable, the adsorbed protons have to be present under experimental conditions. It was previously found that water dissociation on this surface leads to formation of adsorbed protons with hydride character. To our knowledge, no studies have investigated the stability of the adsorbed protons in the presence of other species involved in the proposed mechanism under relevant experimental conditions. As a baseline, we
first computed the $pK_a$ of an adsorbed proton on the bare, neutral surface ($H^+1^*$, Figure 5.4a) and the $pK_a$s of other relevant species. Comparing these $pK_a$s reveals the relative stability of adsorbed protons: species more acidic than $H^+1^*$ will protonate the bare surface while species less acidic will get protonated by adsorbed protons.

We then studied how the $pK_a$ of adsorbed protons is affected by relevant surface features that might vary under experimental conditions, namely proton coverage, surface negative charge, and the presence of co-adsorbed species other than protons. To study the effect of proton coverage, we re-computed the $H^+1^*$ $pK_a$ in the presence of varying numbers of co-adsorbed protons. Because the GaP electrode is held under negative bias in the experiments, we also studied the effect of negatively charging the surface by computing the $H^+1^*$ $pK_a$ in the presence of added electrons. Finally, other species are expected to adsorb on the electrode surface (vide infra). We investigated the effect of species co-adsorption by re-computing the $H^+1^*$ $pK_a$ with varying adjacent co-adsorbed species. In all of these studies, we not only simulated an implicitly solvated bare surface but also an explicitly solvated surface, which we expect to consist of a 50% dissociated water adlayer. We did so by adsorbing the water-hydroxide hydrogen-bonded complexes ($H_2O$-OH$^-$) recently observed on the GaP(110) surface (Chapter 3 and Ref. 10), along with the proton counterions. The explicitly solvated surface was also subjected to the implicit solvation model to simulate the effect of the surrounding water medium.
Figure 5.4 Equilibrium geometries of an adsorbed proton $H^+_1$ in (a) and potential co-adsorbates (b,c,d,e,f,g,h,i) adsorbing next to it on the bare, neutral surface of the GaP cluster. The potential co-adsorbates considered in this study are: (b) $H_2O$, (c) $OH^-$, (d) $H_2O$ and $OH^-$ adjacently co-adsorbed as a hydrogen-bonded complex, (e) pyridine (Py), (f) Py and $H_2O$ adjacent co-adsorbed, (g) Py and $OH^-$ adjacent co-adsorbed, (h) 1,2-(ortho)-dihydropyridine ($o$-DHP), and (i) $HCOO^-$. The co-adsorbates in f and g are displayed at a different angle from the others in order to clearly show both adsorbates.
Table 5.1 $pK_a$ values of a proton adsorbed on the GaP(110) surface on P and Ga adsorption sites and in the presence of zero, one and two extra electrons corresponding to surface charge 0, -1, and -2, respectively. -1 and -2 surface charges correspond to approximate surface charge densities of 0.010e / Å² and 0.020e / Å², respectively, based on the surface area of the cluster model used (96 Å²).

Proton adsorption was always modeled only on P surface sites, as they represent the major adsorption sites for protons. This choice is not only more intuitive but it is also supported by the ambient pressure photoelectron spectroscopy experiments discussed in Chapter 3 and Ref. 10. These experiments showed that when water interacts with the GaP(110) surface, it partly dissociates leading to formation of Ga-OH and P-H species. However, these experiments were performed in the absence of an applied bias. Under this condition, Ga surface states might be occupied by the electrons deriving from the applied negative bias, thus making Ga surface atoms attractive adsorption sites for protons. To test this hypothesis, we computed the $pK_a$ of a proton adsorbed on a Ga surface site in the case of a bare surface when different numbers of extra electrons (corresponding to different values of surface charge, see the caption of Table 5.1) are added to the cluster model and are localized on the Ga adsorption site. These $pK_a$ results are
reported in Table 5.1 where they are also compared to the results for a proton adsorbed on a P surface site:

From Table 5.1, it is clear that adsorption on Ga surface sites is preferred to adsorption on P surface sites only when Ga sites are hosting two extra electrons, which might occur under applied bias. However, as we will discuss in section 6.3.1 of Chapter 6, the negative bias can lead to the occupation of only few Ga surface sites. Therefore, even under applied bias conditions, the P surface sites remain the major adsorption sites for protons and there is no need to consider proton adsorption on Ga sites in this work.

5.3.1 Adsorption of Relevant Species on the Solvated GaP(110) Surface
We identified species for co-adsorption on the context of the experimental conditions and the proposed mechanism. We first determined which species should be directly adsorbed on the electrode surface on the basis of adsorption free energies computed using our implicitly solvated cluster model of a neutral surface (second column of Table 5.2 and Table 5.3). We used the same adsorption free energy definition as reported in section 4.2.2 of Chapter 4. These computed adsorption free energies are in good agreement with previous predictions by our group.\textsuperscript{12} We then proceeded to verify the adsorption free energy trend thus obtained with more accurate calculations. First, adsorption free energies derived using a mixed implicit-explicit solvation approach (for which we used SMD in the presence of a full monolayer of half-dissociated water molecules as described in section 4.2.2 of Chapter 4) yielded largely the same adsorption free energy trend (Table 5.2). This identical result was also obtained in Chapter 4, where we studied a part of the species investigated in this study. The only exception is \textit{o}-DHP for which the
adsorption free energy becomes more favorable with the mixed solvation approach. We have already discussed a possible reason for this exception in section 4.8 of Chapter 4.

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption free energy (kcal/mol) at 298.15 K</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Implicit solvation</td>
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<tr>
<td>PyH⁺</td>
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</tr>
<tr>
<td>CO₂</td>
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</tr>
<tr>
<td>HCOOH</td>
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</tr>
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</tr>
<tr>
<td>Py</td>
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</tr>
<tr>
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<tr>
<td>OH⁻</td>
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</tr>
<tr>
<td>H₂O⁺H⁺</td>
<td>-25.5</td>
</tr>
</tbody>
</table>

Table 5.2 Adsorption free energies of relevant species (pyridinium (PyH⁺), CO₂, HCOOH, H₂O, 1,2-(ortho)-dihydropyridine (o-DHP), pyridine (Py), HCOO⁻, OH⁻, H₂O⁺H⁺) on the solvated GaP cluster model at 298.15 K computed using both the implicit and the mixed implicit-explicit solvation schemes. Unlike the rest of the species that adsorb molecularly intact, H₃O⁺ adsorption is dissociative and produces adjacently adsorbed H₂O⁺H⁺ (hence the adsorbate entry in column 1 is shown as the latter species). Thus the H₃O⁺ adsorption free energy was computed with Gₓ taken as the free energy of implicitly solvated H₃O⁺. The data reported for PyH⁺, CO₂, H₂O, o-DHP and Py are the same as the data reported in Table 4.3 of Chapter 4.
<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption free energy (kcal/mol) at 298.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface charge=0</td>
</tr>
<tr>
<td>PyH⁺</td>
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</tr>
<tr>
<td>CO₂</td>
<td>+2.5</td>
</tr>
<tr>
<td>HCOOH</td>
<td>-0.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>-2.0</td>
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<tr>
<td>o-DHP</td>
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<td>Py</td>
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<tr>
<td>H₂O+H⁺</td>
<td>-25.5</td>
</tr>
</tbody>
</table>

Table 5.3 Adsorption free energies of relevant species (pyridinium (PyH⁺), CO₂, HCOOH, H₂O, 1,2-(ortho)-dihydropyridine (o-DHP), pyridine (Py), HCOO⁻, OH⁻, H₂O+H⁺) on the neutral and negatively charged implicitly solvated GaP cluster model at 298.15 K. Surface charges -1 e and -2 e were simulated by adding one and two extra electrons to the system, respectively; these correspond to approximate surface charge densities of 0.010e / Å² and 0.020e / Å², respectively, based on the surface area of the cluster model used (96 Å²). The data reported for PyH⁺, CO₂, H₂O, o-DHP and Py are the same as the data reported in Table 4.4 of Chapter 4.

Next, we verified that this same adsorption free energy trend mostly holds when extra electrons are added to simulate the negatively charged p-GaP photocathode surface (Table 5.3). Given that largely the same adsorption free energy trend is found with both solvation approaches, we therefore decided to only use the implicit solvation scheme to study the effect of
electrode negative charge on the adsorption free energies. Again, roughly the same adsorption free energy trend predicted for the neutral surface holds for the negatively charged surface, with HCOO\(^-\) being an exception in the case of addition of two electrons to the cluster model. This exception is readily explained given the large electrostatic repulsion between HCOO\(^-\), a bidentate adsorbate, and the negatively charged surface.

In the experiment, the p-GaP photocathode is in contact with an acidified aqueous solution (pH 5.2) containing Py. Given the Py p\(K_a\) (5.3) and the experimental pH (5.2), about half of the Py will be in its protonated form PyH\(^+\). Consequently, we expect protons (H\(_3\)O\(^+\)), Py, PyH\(^+\), and H\(_2\)O to exist in solution. The following conclusions regarding which species will adsorb on GaP are gleaned from Table 5.2 and Table 5.3. H\(_2\)O is expected to be weakly adsorbed on the surface while Py is more strongly adsorbed, suggesting that Py may readily exchange with water at the electrode surface. By contrast, PyH\(^+\) adsorption is not thermodynamically favored and hence we expect it to remain in solution, though its concentration could be higher than average near the negatively charged photocathode due to electrostatic attraction. CO\(_2\) adsorption is not thermodynamically favored and hence it should only exist in solution. H\(_3\)O\(^+\) is predicted to dissociatively adsorb by depositing its excess proton onto a surface P atom and binding the remaining neutral H\(_2\)O to a neighboring Ga atom. During the experiment, CO\(_2\) is bubbled into the system and reduced to methanol. Our models suggest that HCOOH will either adsorb very weakly or not at all and therefore we expect it to be mostly in solution. By contrast, adsorption of OH\(^-\), DHP, and HCOO\(^-\) are all strongly thermodynamically favored; we therefore expect them to exist primarily on the surface rather than in solution.
All species predicted to stably adsorb will be evaluated as potential co-adsorbates below. We also consider other potential co-adsorbates derived from the H$_2$O-OH$^-$ hydrogen-bonded complex adsorbed on GaP(110) identified in the study presented in Chapter 3 and Ref. 10. Py adsorbs ~6 kcal/mol more strongly than H$_2$O and thus might replace the H$_2$O molecule in adsorbed H$_2$O-OH$^-$ for this reason, in addition to evaluating co-adsorbed H$_2$O-OH$^-$, we also consider Py and OH$^-$ as potential co-adsorbates on two neighboring Ga sites (Py-OH$^-$). However, if adsorbed H$_2$O is replaced by a Py in adsorbed H$_2$O-OH$^-$, the adsorbed OH$^-$ will no longer be stabilized by a hydrogen bond with a co-adsorbed H$_2$O molecule and might instead get protonated to form an adsorbed H$_2$O. We therefore also consider Py and H$_2$O as potential co-adsorbates on two neighboring Ga sites (Py-H$_2$O). The adsorption geometries of all of these species are shown in Figure 5.4, together with the adsorption geometry of H$^+_{1*}$. Finally, as discussed in section 4.7 of Chapter 4, two possible isomers of DHP could form (o-DHP and 1,4-(para)-dihydropyridine (p-DHP)), although here we consider only o-DHP for simplicity.

5.3.2 Adsorbed Proton Relative Stability on the Bare, Neutral Surface

To get a first estimate of the relative surface acidity, we computed the pK$_a$ of H$^+_{1*}$ and we compared it to the computed pK$_a$s of protic species that are likely to be present in solution and on the surface (Table 5.4). The pK$_a$ of o-DHP is computed for dissociation of the proton bound to the nitrogen atom.
<table>
<thead>
<tr>
<th>Species</th>
<th>$pK_a$</th>
</tr>
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<tr>
<td><strong>Theory (this work)</strong></td>
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</tr>
<tr>
<td>HCOOH*</td>
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<tr>
<td>H$_2$O$^+$</td>
<td>-3.2</td>
</tr>
<tr>
<td>H$^+_1$*</td>
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<tr>
<td>HCOOH</td>
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<tr>
<td>PyH$^+$</td>
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<td>H$_2$O*</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.8</td>
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<td>15.7</td>
</tr>
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</tr>
</tbody>
</table>

Table 5.4 Comparison of the computed $pK_a$ of an adsorbed proton on the bare, neutral surface of the GaP cluster (H$^+_1$*) with the $pK_a$s (both computed and experimental values when available) of other relevant species (HCOOH, H$_2$O$^+$, pyridinium (PyH$^+$), H$_2$O, 1,2-(ortho)-dihydropyridine ($o$-DHP)). * indicates species adsorbed on the surface. The H$^+_1$* $pK_a$ is calculated for a proton coverage equal to ~0.125 monolayer (ML). Experimental $pK_a$s for HCOOH and PyH$^+$ are taken from Ref. 21. Experimental $pK_a$s for H$_2$O and H$_3$O$^+$ are calculated from the H$_2$O ionic product $K_w$ and molarity of pure H$_2$O.

Several conclusions can be drawn from the $pK_a$s reported in Table 5.4. First, our model captures the correct $pK_a$ trend for molecules with the following known experimental $pK_a$s: H$_3$O$^+$ $pK_a = -1.8 < $ HCOOH $pK_a = 3.8^{21} < $ PyH$^+$ $pK_a = 5.2^{21} < $ H$_2$O $pK_a = 15.7$. In addition, we observe a consistent effect of adsorption: the adsorbed species is always more acidic than the
same species in solution. Adsorption thus effectively weakens the O-H (in HCOOH and H$_2$O) and N-H (in o-DHP) bonds, presumably due to the enhanced stabilization of the resulting deprotonated adsorbate that can more easily form dative bonds to Ga due to reduced steric repulsion. Finally, we can draw two main conclusions based on the relative acidity of surface protons. First, because protons in solution (predicted H$_3$O$^+$ pK$_a$ = -3.2) are more acidic than protons adsorbed on the surface (predicted H$^+$* pK$_a$ = 2.2), the bare, neutral surface will be protonated by protons from solution (or by any weakly adsorbed formic acid). Second, adsorbed protons represent relatively acidic species in this model of the system, as their predicted pK$_a$ (2.2) is lower than the pK$_a$ of many other species potentially involved in the reduction of CO$_2$. This last result suggests that adsorbed protons may be transferred away from the surface and hence may not be available to react with adsorbed Py to generate DHP.

However, these conclusions only apply to the surface with a low proton coverage (~0.125 ML), with zero initial total charge prior to adding protons and with no other species adsorbed. Under experimental conditions, these three surface features (i.e., proton coverage, surface charge, and presence of co-adsorbed species other than protons) will undoubtedly play a role. We therefore are interested in understanding how the relative stability of the adsorbed protons is affected by them. Most importantly, the presence of H$_2$O-OH$^-$ hydrogen-bonded complexes that form at the GaP/water interface (see Chapter 3 and Ref. 10) needs to be taken into account when studying the adsorbed proton relative stability. We considered three possible coverages for the explicitly solvated surface: only one nearby H$_2$O-OH$^-$ complex (H$_2$O-OH$^-$*), two H$_2$O-OH$^-$ complexes (2 H$_2$O-OH$^-$*) and two H$_2$O-OH$^-$ complexes plus three undissociated water molecules (2 H$_2$O-OH$^-$*+3 H$_2$O*) on the cluster model surface. This last coverage best simulates
the aqueous environment present under experimental conditions as it corresponds to a full monolayer coverage (see section 4.2.2 of Chapter 4 for more details).\textsuperscript{10} These coverages are illustrated in Figure 5.5.

Figure 5.5 (a) Top and (b) side views of the GaP(110) surface cluster model with different coverages: bare surface, surface covered by only one H\textsubscript{2}O-OH\textsuperscript{-} complex (H\textsubscript{2}O-OH\textsuperscript{*}), two H\textsubscript{2}O-OH\textsuperscript{-} complexes (2 H\textsubscript{2}O-OH\textsuperscript{*}) and two H\textsubscript{2}O-OH\textsuperscript{-} complexes plus three undissociated water molecules (2 H\textsubscript{2}O-OH\textsuperscript{*}+3 H\textsubscript{2}O\textsuperscript{*}). * indicates species adsorbed on the surface.
5.3.3 Proton Coverage Effect on Adsorbed Proton Relative Stability

To analyze the effect of proton coverage, we recomputed the $H^+_{1^*}$ $pK_a$ in the presence of additional protons co-adsorbed on the implicitly solvated bare surface and on the explicitly solvated one. The addition of protons on the surface is schematically represented in Figure 5.6. The approximate coverages were calculated considering the eight possible P sites for proton adsorption on the cluster surface. Note that Figure 5.6 depicts the surface P sites where protons were adsorbed on the bare surface but protons were adsorbed on the exact same P sites on the explicitly solvated surface. We consider 0.25 ML (i.e., two protons on the surface of the cluster model) as the maximum proton coverage, as this is the proton coverage needed together with two $H_2O$-$OH^-$ complexes and three undissociated water molecules to simulate a full monolayer of half-dissociated water molecules on the surface.

Figure 5.6 Proton adsorption on the GaP(110) cluster model. Proton numbering indicates the order in which protons were added to the cluster in order to simulate increasing coverages (e.g., $H^+_{1^*}$ is the first proton added to the cluster to simulate 0.125 monolayer (ML) coverage and $H^+_{2^*}$ is added to the cluster to simulate 0.25 ML coverage). * indicates species adsorbed on the surface.
Figure 5.7 Effect of proton coverage on adsorbed proton acidity: comparison of the $pK_a$'s of $H^+_1^*$ at ~0.125 monolayer (ML) and ~0.25 ML coverage on the implicitly solvated bare, neutral surface and on the implicitly solvated neutral surface covered by different numbers of $H_2O$-$OH^-*$ complexes and $H_2O^*$ molecules modeling the GaP/water interface. 2 $H_2O$-$OH^-*$ + 3 $H_2O^*$ coverage represents a full monolayer (fully solvated) coverage as this is the maximum number of adsorbates that can be added on the cluster surface. * indicates species adsorbed on the surface.

As proton coverage increases, the $pK_a$ of $H^+_1^*$ is predicted to decrease slightly (Figure 5.7) suggesting that higher proton coverages destabilize adsorbed protons, possibly favoring their transfer to other species. This result is simply explained by electrostatic repulsion between the adsorbed protons that developed a hydride character upon adsorption. The bare and explicitly solvated surfaces with different numbers of $H_2O$-$OH^-$ complexes and $H_2O$ molecules exhibit the same trends. Most striking, however, is the dramatic effect that the adsorption of $H_2O$-$OH^-$...
complexes and H$_2$O molecules has on the surface proton relative stability: the H$^{+1*}$ p$K_a$ increases by more than 9 p$K_a$ units, even when only one H$_2$O-OH$^{-}$ complex is adsorbed on the surface and it increases even further (by ~3 p$K_a$ units) when two H$_2$O-OH$^{-}$ complexes are adsorbed. When full coverage (2 H$_2$O-OH$^{-}$ + 3 H$_2$O$^*$) is reached, the H$^{+1*}$ p$K_a$ decreases slightly from the 2 H$_2$O-OH$^*$ case. At full coverage, the adsorbates (i.e., H$_2$O-OH$^{-}$ complexes and H$_2$O molecules) are forced to re-arrange, with more steric repulsion between adsorbates and the adsorbed protons, rendering the latter a bit less stable.

We can now compare the H$^{+1*}$ p$K_a$ on the fully solvated surface (2 H$_2$O-OH$^{-}$ + 3 H$_2$O$^*$ coverage) and at different proton coverages to the p$K_a$ of other species (Table 5.4) to get a more accurate estimate of the adsorbed proton relative stability. When the surface is fully solvated, the H$^{+1*}$ p$K_a$ at 0.125 ML (13.8) is higher than the p$K_a$ of most other species considered. The only species with a larger p$K_a$ are solvated H$_2$O (p$K_a$ = 17) and solvated o-DHP (p$K_a$ = 22.2), which are unlikely to be deprotonated in the acidic solution used in the experiments. Furthermore, even when the proton coverage is higher (0.25 ML), the only species with a higher p$K_a$ than H$^{+1*}$ (now 11.5) are adsorbed o-DHP (p$K_a$ = 13.4), solvated H$_2$O (p$K_a$ = 17) and solvated o-DHP (p$K_a$ = 22.2). Overall, in contrast to proton stability on the bare surface, we predict that adsorbed protons are extremely stable in the aqueous environment present under experimental conditions.

5.3.4 Surface Negative Charge Effect on Adsorbed Proton Relative Stability

To analyze the effect of GaP photoelectrode surface negative bias, we recomputed the H$^{+1*}$ p$K_a$ when extra electrons are added both to the implicitly solvated bare surface and to the explicitly solvated surface. For both the implicitly solvated bare and the mixed implicitly/explicitly solvated surfaces, negatively charging the surface decreases its acidity (Figure 5.8) because the
added electrons simply promote adsorption of protons (charge compensation). We therefore conclude that the stability of surface protons is increased by the negative charge on the photocathode. The presence of H₂O-OH⁻ and H₂O adsorbates further stabilizes the protons adsorbed on the surface. Overall, when accounting for both the presence of these water-derived adsorbates and the surface negative charge, the H⁺₁⁻* pKₐ is predicted to be higher than the adsorbed o-DHP pKₐ (13.4), suggesting that the protons needed for adsorbed DHP formation will have to be provided by another source such as the acidified aqueous solution.

Figure 5.8 Effect of negatively charging the surface on adsorbed proton acidity: comparison of the H⁺₁⁻* pKₐs at a coverage of ~0.125 monolayer (ML) on neutral and negatively charged surfaces in the absence and presence of different numbers of H₂O-OH* complexes and H₂O* molecules. Surface charges -1 e and -2 e were simulated by adding one and two extra electrons to the system, respectively; these correspond to approximate surface charge densities of 0.010e / Å² and 0.020e / Å², respectively, based on the surface area of the cluster model used (96 Å²).
5.3.5 *Surface Negative Charge and Proton Coverage Cumulative Effect on Adsorbed Proton Relative Stability*

We also studied the simultaneous effect of proton coverage and photoelectrode negative charge. Figure 5.9 displays predicted H$^{+}\cdot$ $pK_a$s for different conditions of proton coverage and surface charge for both the implicitly solvated bare surface and the implicitly solvated fully hydrated surface. Specifically, we considered our two proton coverages (0.125 and 0.25 ML) and our three surface charges (0, -1, and -2 e). We showed above that when the surface is neutral (Figure 5.7), a higher proton coverage disfavors further proton adsorption (i.e., the H$^{+}\cdot$ $pK_a$ decreases) because of electrostatic repulsion. In the case of the implicitly solvated, bare, negatively charged surface (Figure 5.9a) we see the opposite trend: a higher coverage of protons is favored due to the additional electron density in the surface attracting the positively charged protons. By contrast, in the case of the fully hydrated surface (Figure 5.9b), a higher proton coverage has the same effect for the neutral and the negatively charged surface: a higher proton coverage destabilizes the adsorption of protons (i.e., the H$^{+}\cdot$ $pK_a$ is lower at 0.25 ML than at 0.125 ML).

The different effect of proton coverage on the H$^{+}\cdot$ $pK_a$ for the bare, negatively charged surface and the fully hydrated, negatively charged surface can be explained by localization of the added electron(s). In the case of the bare, negatively charged surface, the extra electron(s) localize on a Ga surface site near the adsorbed protons, thus strongly stabilizing them and favoring a higher proton coverage. In the case of the fully hydrated, negatively charged surface, the Ga surface sites near the adsorbed protons are saturated by adsorbed OH$^-$ and H$_2$O molecules and thus cannot host the extra electron(s). Therefore, the adsorbed protons are less stabilized by the surface negative charge and electrostatic repulsion among the former dominates.
Figure 5.9 Effect of surface charge and proton coverage on adsorbed proton acidity: comparison of $\text{H}^+\text{pK}_a$s at different proton coverages (monolayer (ML)) and different surface charges on both (a) the implicitly solvated bare surface and (b) the implicitly solvated surface fully covered by 2 H$_2$O-OH$^-$ and 3 H$_2$O adsorbates (1 ML of water, 50% dissociated). Surface charges -1 e and -2 e were simulated by adding one and two extra electrons to the system, respectively; these surface charges correspond to approximate surface charge densities of 0.010e/Å$^2$ and 0.020e/Å$^2$, respectively, based on the surface area of the cluster model used in this work (96 Å$^2$).

5.3.6 Species Co-Adsorption Effect on Adsorbed Proton Relative Stability

As discussed above, several species are expected to adsorb on the electrode surface according to the adsorption free energies computed in previous studies$^{9,12}$ and here (Table 5.2 and Table 5.3): H$_2$O, o-DHP, Py, OH$^-$, and HCOO$^-$, along with the H$_2$O-OH$^-$ hydrogen-bonded complexes that might lead to formation of Py-OH$^-$ and Py-H$_2$O co-adsorbates on neighboring Ga sites. It is therefore important to study how the adsorption of all of these isolated and co-adsorbed species affects the acidity of adsorbed protons. In Table 5.5, we report the $\text{H}^+\text{pK}_a$ computed in the absence and presence of these species co-adsorbed next to it. We only considered adsorbed
HCOO$^-$ and not the very weakly adsorbed HCOOH, since the latter will likely be deprotonated under the experimental conditions, given its low $pK_a$ (Table 5.1) and that HCOO$^-$ adsorption is strongly favored. Table 5.5 reveals that co-adsorption of any of these species increases the $H^+_{1*} pK_a$. The explanation is simple: their dative bonding to the surface introduces extra electron density that promotes proton adsorption. Furthermore, comparing the $H^+_{1*} pK_a$ in the presence of multiple versus isolated co-adsorbates indicates that this proton stabilization effect is additive: when multiple species co-adsorb next to $H^+_{1*}$ (i.e., H$_2$O-OH$^-$, Py-OH$^-$, and Py-H$_2$O co-adsorbates), the $H^+_{1*} pK_a$ is approximately equal to the sum of $H^+_{1*} pK_a$'s computed when the corresponding individual species are adsorbing next to it (i.e., H$_2$O and OH$^-$, Py and OH$^-$, and Py and H$_2$O). This stabilization is predicted to be a local effect: a substantial $pK_a$ increase is only observed when the co-adsorbing species is on a neighboring site (i.e., a Ga surface site directly bound to a P surface site hosting the proton, as shown in Figure 5.4). For instance, if Py adsorbs on a non-neighboring Ga site, the $H^+_{1*} pK_a$ is only 2.5 instead of 4.5 when Py adsorbs on a neighboring site. Thus, protons will most favorably adsorb near species adsorbing via dative bonding such as Py because they are more stable (i.e., less acidic) under these conditions. This finding is very relevant in the context of the proposed mechanism in which the adsorbed protons react with adsorbed Py to form DHP.

Overall, the effect of species co-adsorption is to favor proton adsorption (i.e., the $H^+_{1*} pK_a$ is higher) near adsorbed H$_2$O-OH$^-$ hydrogen-bonded complexes and even more near Py-OH$^-$ co-adsorbates. The surface likely will be covered by these adsorbates under experimental conditions. Furthermore, under experimental conditions the surface will be negatively charged; Figure 5.8 already revealed that a negatively charged surface, in the presence of a full hydration layer, will further stabilize the adsorbed protons.
<table>
<thead>
<tr>
<th>Co-adsorbed species</th>
<th>$H^+_{1*} pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>2.2</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>3.4</td>
</tr>
<tr>
<td>$o$-DHP</td>
<td>4.0</td>
</tr>
<tr>
<td>Py</td>
<td>4.5</td>
</tr>
<tr>
<td>Py-$H_2O$</td>
<td>6.7</td>
</tr>
<tr>
<td>$OH^-$</td>
<td>8.5</td>
</tr>
<tr>
<td>$HCOO^-$</td>
<td>9.2</td>
</tr>
<tr>
<td>$H_2O-OH^-$</td>
<td>11.5</td>
</tr>
<tr>
<td>Py-$OH^-$</td>
<td>12.1</td>
</tr>
</tbody>
</table>

Table 5.5. Comparison of the $H^+_{1*} pK_a$ in the absence and presence of other co-adsorbates ($H_2O$, 1,2-(ortho)-dihydropyridine ($o$-DHP), pyridine (Py), Py-$H_2O$, $OH^-$, $HCOO^-$, $H_2O-OH^-$, Py-$OH^-$). All isolated species co-adsorb on a Ga adsorption site directly bound to the P site where $H^+_{1*}$ adsorbs, as shown in Figure 5.4. Co-adsorbed species adsorb on the two Ga adsorption sites directly bound to the P adsorption site where $H^+_{1*}$ adsorbs, as shown in Figure 5.4.

5.3.7 Discussion

We aim to gain new insights into Py-catalyzed CO$_2$ reduction on p-GaP photoelectrodes. Here, we specifically test one aspect of a proposed heterogeneous mechanism in which adsorbed DHP is the active catalyst (Figure 5.1).$^{7,8}$ Formation of adsorbed DHP by the reaction between adsorbed Py and adsorbed protons that develop hydride character is a key proposed step. One necessary but not sufficient condition is that the adsorbed protons are stable under experimental
conditions. In the previous section, we assessed under different conditions how easily protons adsorb on the GaP surface and how stable they are towards proton transfer, by using their pK_a as a metric.

Protons adsorbing on the neutral, bare GaP(110) surface are relatively acidic (predicted H^+_1 pK_a=0.7 at ~0.25 ML) suggesting that they might be unstable and easily transferred to other species approaching the surface. However, in the experimental setup, GaP is biased slightly negative so its surface is slightly negatively charged. Moreover, under experimental conditions, the GaP(110)/water interface will be fully hydrated by adsorbed H_2O-OH^- hydrogen-bonded complexes (Chapter 3 and Ref. 10). When the surface is fully covered by these species, the adsorbed protons are greatly stabilized (with an increase in H^+_1* pK_a by more than 10 pK_a units with respect to the bare surface) and higher proton coverages are favored. Furthermore, when the surface is negatively charged, the acidity of the surface protons strongly decreases and again higher proton coverages are favored, for both bare and fully hydrated surfaces. The aqueous environment and the negative charge of the photocathode thus will strongly increase the stability of surface protons, limiting their transfer to other species approaching the surface. Proton adsorption is predicted to be favored in the presence of any species co-adsorbing via dative bonding on neighboring sites. One of the most favorable proton adsorption sites is near an adsorbed H_2O-OH^- hydrogen-bonded complex (H^+_1* pK_a = 11.5), which will be present on the surface when immersed in aqueous solution. Based on our computed adsorption free energies, we predict that Py can replace adsorbed H_2O molecules in these H_2O-OH^- hydrogen-bonded complexes and Py-OH^- co-adsorbates might form; proton adsorption on a P site near these co-adsorbates is even more favorable (H^+_1* pK_a = 12.1). However, Py-H_2O co-adsorbates might form by protonation of the Py-OH^- co-adsorbates. If this occurs, the adsorbed protons adjacent to
these co-adsorbates will be less stabilized (H⁺ i* pKₐ = 6.7) but will still be less acidic than many other species present, especially when taking into account the extra stabilization that will result from the photocathode negative charge (-0.2 to -0.7 V applied bias in the experiments).

Overall, under experimental conditions, protons will adsorb on the surface and their transfer to other species will be limited, given the stabilization provided by surface negative charge and the aqueous environment. These findings have two main implications for the proposed heterogeneous mechanism on GaP(110). First and most importantly, these results clearly imply that adsorbed protons will be stable and available to be reduced to adsorbed hydrides on the GaP (110) surface either through negative biasing or under illumination that produces energetic (photoexcited) electrons. Therefore, the proposed mechanism, which relies on the availability of these species for formation of the active catalyst, is partly validated. Second, the stability of the surface protons also suggests that they are unlikely to protonate other species under electrochemical conditions. Consequently, protons involved in any mechanism producing adsorbed DHP probably originate from a proton source other than the surface, such as the acidified aqueous solution in contact with the electrode.

We have argued at the beginning of the Results and discussion section that P surface sites are the sites for protons, and we therefore have only modeled proton adsorption on P sites in this study. We now additionally note that, even if the applied bias was to favor proton adsorption on a non-negligible number of Ga sites, the large, positive pKₐ (28.0) suggests that our main conclusion does not change: adsorbed protons are very stable under experimental conditions and can potentially be reduced to hydrides and react to form the proposed active catalyst DHP.
5.4 Conclusions

A first step has been taken towards testing the proposed heterogeneous mechanism for CO$_2$ reduction catalyzed by DHP on GaP(110). In this mechanism, surface protons that develop hydride character via adsorption at P surface sites play a crucial role, as they are postulated to be directly involved in the formation of the proposed active catalyst, adsorbed DHP (Figure 5.1). We studied the relative stability of these adsorbed protons using cluster models with dispersion-corrected DFT and continuum (as well explicit) solvation to calculate their pK$_a$s and compared them to the computed pK$_a$s of other relevant species. We investigated how the acidity of the adsorbed protons is affected by proton coverage and typical experimental conditions, namely photocathode negative charge, species at the semiconductor/water interface, and presence of relevant species adsorbing on neighboring surface sites. We conclude that adsorbed protons are very stable under these conditions, especially when adsorbing near adsorbed hydroxide-water hydrogen-bonded complexes, species that were already determined to form at the water/GaP interface (Chapter 3 and Ref. 10). Specifically, the pK$_a$ of an adsorbed proton increases by more than 10 pK$_a$ units on the fully hydrated and slightly negatively charged surface. This result suggests that the previously identified adsorbed protons with hydride character deriving from water dissociation are very stable under experimental conditions. As a consequence, we expect the photocathode surface to have a relatively high proton coverage (0.25 ML) that potentially could enable the proposed mechanism for DHP formation by providing a hydride source under negative bias and illumination that produces a source of reducing electrons. On the other hand, the high stability of these species also suggests that the surface does not represent a significant proton source and therefore the protons required for adsorbed DHP formation will likely come from solution rather than the electrode surface.
5.5 References


Chapter 6

Role of Pyridinium and the p-GaP Photoelectrode Surface in Pyridine-Catalyzed CO2 Reduction‡‡

6.1 Introduction

In Chapter 1 we discussed how experimental observations suggest that both pyridinium (PyH+) and the electrode surface might play a role in the pyridine (Py)-catalyzed mechanism of CO2 reduction. First, in an earlier set of experiments using Pd electrodes, Bocarsly and co-workers found that no reduction occurred at pH values higher than 7.1 From this observation, they concluded that the acidic environment is required for catalyzing the reduction of CO2 using Py. More specifically, PyH+, which is present in significant concentration at acidic pH given its pK_a (5.3), may play an important role in the catalysis. Second, several experimental studies employing different electrodes have reported varying results in terms of selectivity and required potential,1–6 which suggests that the nature of the electrode surface might play a non-trivial role. Thus, the objective of this chapter is to further investigate the role of PyH+ and the surface, thereby elucidating the overall catalytic mechanism.

As discussed in Chapter 1, the role of PyH+ has been investigated previously with different hypotheses formulated. Here, we briefly summarize these hypotheses and findings that motivate our study. The experimental evidence suggests that PyH+ might play an important role

‡‡ Portions of this chapter were adapted from the following papers with permission:
in the catalysis, so PyH⁺ reduction to the 1-pyridinyl radical (1-PyH⁺) was proposed as a crucial mechanistic step in two studies: Bocarsly and co-workers originally conjectured that 1-PyH⁺ itself is the active catalyst for CO₂ reduction (see section 1.3.2 of Chapter 1 for more details on this proposed mechanism),³ while Musgrave and co-workers more recently proposed that 1-PyH⁺ will further react to form dihydropyridine (DHP) as the active (homogeneous) catalyst (see section 1.3.2 of Chapter 1 for more details on this proposed mechanism).⁷ However, as discussed in Chapter 1, first principles quantum mechanics studies⁸–¹¹ showed that PyH⁺ reduction to 1-PyH⁺ is energetically unfeasible in solution when using metal electrodes and under the experimentally applied potential (∼-0.58 V vs. saturated calomel electrode (SCE) on Pt electrodes³). In contrast, Musgrave and co-workers argued that PyH⁺ may be reduced to 1-PyH⁺ when using p-GaP photoelectrodes because the photoexcited electrons might have enough energy.⁷ However, recent cluster calculations by our group investigating the GaP(110) surface suggested that the transfer of photoexcited electrons from the GaP surface to PyH⁺ is not favorable.¹² Furthermore, these calculations also showed that PyH⁺ will not directly adsorb on the surface, preferring to be in solution, suggesting that the reduction process cannot be facilitated by adsorption. This finding in regards to unfavorable PyH⁺ adsorption is also confirmed by our study with both the neutral and negatively charged solvated cluster models reported in Chapter 4. These are crucial findings towards elucidating the mechanism of CO₂ reduction in this promising system. However, a more accurate investigation is needed to confirm or to exclude the possibility of PyH⁺ reduction to 1-PyH⁺ by photoexcited electrons from the p-GaP photocathode.

The mechanism proposed by Bocarsly and co-workers³ and the mechanism proposed by Musgrave and co-workers⁷ are both homogeneous; as such, they do not provide any role for the
electrode surface except for being the source of photoexcited electrons. In contrast, the mechanism proposed by Keith and Carter\cite{13,14} is heterogeneous and thus requires an active participation of the surface via formation and reaction of an adsorbed active catalyst. Therefore, understanding whether or not the surface plays a role is necessary to establish the validity of previously proposed mechanisms and to hypothesize new alternative ones.

In this chapter, we address the hypothesis of 1-PyH$^\cdot$ formation via PyH$^+$ reduction by using more accurate methods to further test the results of previous cluster calculations.\cite{12} We first study 1-PyH$^\cdot$ in contact with the surface via electron density difference and charge analyses to investigate the previously predicted electron transfer from the radical to the surface.\cite{12} We then compute the conduction band minimum (CB$_\text{min}$) of the GaP(110) surface to understand whether or not our results are consistent with the reducing power of the photoexcited electrons provided by the p-GaP electrode under illumination. In addition, we propose a new pathway for PyH$^+$ reduction on p-GaP photocathodes, and we test its feasibility by computing its reduction potential and comparing it to GaP(110) CB$_\text{min}$. We also compare the CB$_\text{min}$ of the GaP(110) and GaP(111) surfaces as well as reduction potentials and adsorption free energies calculated for each surface, with the goal of explaining the experimentally observed difference in activity between them.\cite{15} This analysis provides further evidence to support the hypothesis that the mechanism of CO$_2$ reduction in this system must be a heterogeneous one.

6.2 Computational Approach

Our computational approach uses both finite cluster calculations and periodic boundary condition (PBC) calculations to model the GaP(110) surface and possible adsorbates, as needed to compute different properties. As discussed in section 3.1 of Chapter 3, the GaP(110) surface
was selected because it represents the most stable\textsuperscript{16} and most active surface of GaP.\textsuperscript{15} PBC calculations were used to investigate the stability of the 1-PyH\textsuperscript{•} radical in contact with the GaP(110) surface via electron density difference and charge analyses. A similar study was also conducted with solvated cluster model calculations. Additionally, cluster calculations were used to calculate reduction potentials associated with possible reduction pathways of PyH\textsuperscript{+} on GaP(110), while PBC calculations were used to calculate the CB\textsubscript{min} of the GaP(110) surface to be compared to these reduction potentials.

6.2.1 Periodic Boundary Condition Calculations
We performed all PBC calculations using density functional theory (DFT) with the Vienna Ab initio Simulation Package (VASP) code.\textsuperscript{17–19} All nuclei and electrons were simulated as described in section 4.2.1 of Chapter 4, and all the calculations were performed spin-polarized. We used different unit cell sizes and different k-point sampling grids depending on the specific application (\textit{vide infra}). With these computational parameters and other reported in the following paragraphs, the total energy was always converged to within 1 meV per atom.

The electron density difference plots used to investigate the stability of the 1-PyH\textsuperscript{•} radical in contact with the surface were computed by plotting the following electron density difference:

\[
\rho(\text{GaP} + 1\text{PyH}^\bullet) - \rho(\text{GaP}) - \rho(1\text{PyH}^\bullet)
\]  

where \(\rho(\text{GaP} + 1\text{PyH}^\bullet)\) is the electron density of the GaP(110) periodic slab + 1-PyH\textsuperscript{•} complex, \(\rho(\text{GaP})\) is the electron density of the GaP(110) periodic slab, and \(\rho(1\text{PyH}^\bullet)\) is the electron density of the isolated 1-PyH\textsuperscript{•} radical.
We used the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional with the same periodic slab model and computational details as reported in section 4.2.1 of Chapter 4 for the study of Py and DHP adsorption on GaP(110). The density difference analysis was performed with and without explicit solvation of the surface. The explicitly solvated GaP(110) surface was modeled by including a full monolayer of half-dissociated water molecules adsorbed on the GaP(110) periodic slab model. The employed water configuration was found in our previous study reported in Chapter 3 and Ref. 21 to be the most stable structure of the GaP(110)/water interface. We placed only one adsorbate per surface in each unit cell, leading to a 1/12 monolayer coverage. In the presence of explicit solvation, the radical was placed on top of the adsorbed water monolayer without removing any of the adsorbed water molecules.

We verified that the structures found for the GaP-1-PyH• complex corresponded to true energy minima by performing a vibrational frequency analysis and finding no imaginary frequencies. Given the large number of atoms in the unit cell, we considered all the adsorbate atoms but only a limited number of the surrounding atoms for the vibrational frequency analysis. Specifically, in the case of 1-PyH• adsorbed on the bare periodic slab, we considered the slab atoms directly interacting with the adsorbate, their nearest neighbors, and their next-nearest neighbors within a 4 Å radius from the adsorbate for a total of 4 Ga atoms and 5 P atoms. This is the same criterion that was applied in the study of Py and DHP adsorption in Chapter 4. In the case of 1-PyH• adsorbed on the explicitly solvated GaP(110) surface, we limited the number of atoms included in the vibrational frequency calculation to the 1-PyH• atoms and the atoms belonging to the adsorbed water molecules surrounding 1-PyH• within a 4 Å radius (i.e., two adsorbed H₂O molecules, three adsorbed OH⁻ and one adsorbed proton, for a total of five O
atoms and eight H atoms). The frequencies were computed as described in section 4.2.1 of Chapter 4.

The Bader charge analysis\textsuperscript{22,23} was performed to further investigate the postulated electron transfer between 1-PyH\('\) and the GaP(110) surface. This analysis was conducted using the same parameters and periodic slab model used for the electron density difference analysis from PBC calculations. We used the PBE XC functional\textsuperscript{20} and also tested the PBE0 XC functional only in the case of the GaP-1-PyH\('\) complex without explicit solvation of the surface.\textsuperscript{24} Note that while the geometry was relaxed with the PBE XC functional, we only performed a single point calculation with the PBE0 XC functional given the high computational cost of the hybrid calculation. Furthermore, given the large size of the system under study (144 atoms in the unit cell), we were able to run the PBE0 calculation only with a moderate precision on the fast Fourier transform (FFT) grid for the exact exchange (PRECFOCK tag in VASP). However, a test done with a smaller system revealed that a lower accuracy of the FFT grid for the exact exchange does not significantly affect the atomic charge values computed with the Bader analysis. For this test, we used a hydrogen atom adsorbed on GaP(110) simulated with a smaller periodic slab model for a total of 58 atoms in the unit cell. This system was chosen as a test system because it is also characterized by a net charge transfer between the GaP periodic slab and the adsorbate. In Table 6.1, we report the results of the Bader charge analysis performed on this test system with lower (PRECFOCK=Fast) and higher (PRECFOCK=Normal) precision on the FFT grid for the exact exchange. With both settings of PRECFOCK, we obtained the same exact result in terms of charge transfer.
Table 6.1 Bader charge analysis of a hydrogen atom adsorbed on GaP(110) performed using an electron density obtained with different settings of the PRECFOCK tag in VASP. Table adapted from Ref. 25. Copyright 2015 American Chemical Society.

Accurate band edge positions for the GaP(110) surface were computed following the procedure proposed by Toroker et al.,²⁶ which requires computation of the band gap center (BGC) position with respect to the vacuum level and separately of the band gap. For this reason, we used both DFT (with the PBE XC functional) and the non-self-consistent GW method ($G_0W_0$). The BGC position was simply derived from the work function, which is calculated using a periodic slab model. For this purpose, we used the same slab model and computational parameters as described in section 3.2.1 of Chapter 3 for the study of the GaP(110)/H₂O interface. The work function was computed using both the bare slab and the explicitly solvated slab with one adsorbed monolayer of half-dissociated water molecules. The band gap was calculated using accurate $G_0W_0$ calculations on the GaP bulk phase. In these calculations, we used the primitive cell of GaP that contains only two atoms and thus reduces the computational cost. We first performed a PBE calculation to get a good guess for the wave function to be used as input for the $G_0W_0$ calculations. In these calculations, the Brillouin zone was sampled with a Γ-point-centered 8x8x8 k-point grid. We used 192 bands and the number of frequency points
(NOMEGA tag in VASP) in the G0W0 calculation was set equal to 64. With these computational settings, we reached convergence of the band gap value to within 0.1 eV.

6.2.2 Solvated Cluster Model Calculations

All cluster calculations were performed with the same computational details and cluster model as described in section 4.2.2 of Chapter 4.

The electron density difference plot from cluster calculations was generated by plotting the electron density difference described by Eq. (6.1) where, in this case, $\rho(GaP)$ is the electron density of the GaP(110) solvated cluster model.

Reduction potentials were computed from the reaction free energy in solution ($\Delta G_{aq}$) using the following equation:

$$E^0 = -\Delta G_{aq}/nF$$  \hspace{1cm} (6.2)

where $E^0$ is the reduction potential, $n$ is the number of electrons involved in the reduction process, and $F$ is the Faraday constant. $\Delta G_{aq}$ is often computed using a thermodynamic cycle. However, as discussed in section 5.2 of Chapter 5, a recent study using the Solvation Model based on solute electron Density (SMD)\textsuperscript{27} showed that we can directly compute $\Delta G_{aq}$, saving computational time but without incurring in significant errors on the computed reduction potential values.\textsuperscript{28} Thus, in this work we used the direct approach and $\Delta G_{aq}$ for a generic reduction process $Ox + 1e^- \rightarrow Red$ was computed using the following equation:

$$\Delta G_{aq} = G_{aq}(Red) - G_{aq}(Ox) - G_{aq}(e^-)$$  \hspace{1cm} (6.3)
where $G_{aq}$ is the free energy in solution at room temperature. $G_{aq}(e^-)$ was set equal to -104.3 kcal/mol. This value comes from the absolute potential of the standard hydrogen electrode (SHE, -4.281 V) shifted by -0.244 V to reference our reduction potential values vs. SCE and converted to kcal/mol. Thermal corrections at room temperature were computed as described in section 4.2.2 of Chapter 4.

In this chapter, we will compare our computed reduction potentials for heterogeneous reactions occurring at the GaP(110) surface to the reduction potentials obtained for the GaP(111) surface with implicit solvation only by Dr. Thomas P. Senftle, a current postdoctoral research associate in our group. For this reason, we will not use our mixed implicit-explicit solvation approach of the cluster surface (section 4.2.2 of Chapter 4) when computing the reduction potentials. However, we do not expect this choice to affect our conclusions because, as we will show in Chapter 7, the two solvation approaches give the same trend of reduction potentials.

For the purpose of comparing the computed reduction potentials to the GaP(110) CB$_{min}$, we report these quantities both on the vacuum and on the electrochemical (SCE) scale. Reduction potentials on the SCE scale ($E_{SCE}^0$) were converted to the vacuum scale ($E_{Vacuum}^0$) by using the following equations:

$$E_{SHE}^0 = E_{SCE}^0 + 0.244 \text{ V}$$

(6.4)

$$E_{Vacuum}^0 = -4.281 \text{ V} - E_{SHE}^0$$

(6.5)

where $E_{SHE}^0$ is the reduction potential vs. SHE, and -4.281 V is the absolute potential of the SHE$^{29}$ as discussed above. We used analogous equations to convert the CB$_{min}$ in vacuum to the position on the electrochemical (SCE) scale.
6.3 Results and Discussion

6.3.1 Interaction of the Pyridinyl Radical with the GaP(110) Surface

Previous work employed a simple electron density difference plot to propose that reduction of PyH⁺ to 1-PyH⁺ by photoexcited electrons from the GaP electrode is unlikely to occur.¹² The electron from 1-PyH⁺ spontaneously moved to GaP, with no minimum found for it to stay on 1-PyH⁺. Here, we conducted the same electron density difference analysis with both our cluster approach and PBC calculations (Figure 6.1). As discussed in section 2.3.2 of Chapter 2, the cluster approach is typically used because it allows one to easily simulate solvation effects with a continuum solvation model. However, it has the intrinsic drawback of failing to describe the electronic structure of a periodic crystal, which is a serious issue when studying electron transfer from or to solid materials. This motivated us to verify the cluster calculation result with PBC calculations.

Our cluster calculation result (Figure 6.1a) is identical to the one reported in previous work¹² despite the difference in solvation model (previous work used the CPCM solvation model³⁰) and cluster geometry (see section 4.2.2 of Chapter 4). This indicates that conclusions drawn from these results are robust. Most importantly, the density difference plot generated using DFT PBC calculations with the PBE functional (Figure 6.1b) also yields the same result: a net decrease of electron density surrounding 1-PyH⁺ and an increase of electron density at the GaP surface. The only difference between the two plots is the degree of localization of the electron density at the GaP surface upon transfer of the electron from 1-PyH⁺. While the electron is localized around a single Ga atom at the edge of the cluster in the plot generated with the solvated cluster model (Figure 6.1a), the electron is delocalized around surface atoms close to the 1-PyH⁺ radical in the plot generated with the periodic approach (Figure 6.1b). Overall, our PBC
calculations confirm the result of previous and current cluster calculations: \textit{1-PyH}^+ transfers its electron to the GaP(110) surface.

![Figure 6.1](image)

Figure 6.1 Electron density difference plots showing formation of pyridinium (PyH\(^+\)) and transfer of an electron to the GaP(110) surface simulated with (a) a cluster model and (b) a periodic slab. Ga atoms are represented in blue, P atoms in green, C atoms in violet, N atoms in light blue, and H atoms in white. Increase in electron density is represented in yellow, while decrease is represented in light blue. Isosurface level= (a) 0.002 e/bohr\(^3\), (b) 0.001 e/bohr\(^3\). Figure adapted from Ref. 25. Copyright 2015 American Chemical Society.

To further support the result obtained with the density difference analysis, we performed a Bader charge analysis\(^{22,23}\) on the periodic (GaP-1-PyH)\(^+\) system represented in Figure 6.1b. For this analysis, we solved for the ground-state density using both PBE and PBE0 functionals. Pure DFT notoriously overestimates the extent of charge transfer due to its lack of exact exchange energy. Thus, the hybrid functional PBE0 was used to ensure that our conclusions are not affected by spurious results obtained with the pure PBE functional. Bader charge analysis, performed with both functionals, reveals a net transfer of 0.45e negative charge from the 1-PyH\(^+\)
radical to the GaP slab, independent of functional. This finding suggests that the electron could somehow be shared between the adsorbate and the slab. However, we think this is a spurious result due to the volume assignment in the Bader charge analysis. In fact, in the Bader charge analysis, the resulting charge for each atom depends on the volume assigned to the latter because the charge is calculated by integrating the electron density distributed in this volume.

Figure 6.2 (a) Sum of Bader volumes (yellow isosurface) of the 1-pyridinyl radical (1-PyH⁺) atoms on the GaP(110) surface. (b) Sum of Bader volumes (yellow isosurface) of the surface atoms of the GaP(110) surface. Ga atoms are represented in blue, P atoms in green, C atoms in violet, N atoms in light blue, and H atoms in white. Isosurface level= 0.001e/bohr³. Figure adapted from Ref. 25. Copyright 2015 American Chemical Society.

To further investigate this aspect, we plotted and analyzed the sum of the Bader volumes associated with 1-PyH⁺ atoms and the sum of the Bader volumes of all the surface atoms. These results are reported in Figure 6.2. From this figure, it can be seen that the total Bader volume associated with 1-PyH⁺ (Figure 6.2a) is “embedded” in the total Bader volume associated with surface atoms (Figure 6.2b). This indicates that part of the electron density that should have been attributed to the surface was likely attributed to 1-PyH⁺ which results in an apparent limited charge transfer (only 0.45e). The Bader charge analysis therefore must be considered a lower
bound on the degree of charge transfer. Consistent with this finding, both Mulliken and Löwdin charge analyses of our cluster model give rise to respectively 0.97e and 1.00e charge transfer from the adsorbate to the surface. We therefore conclude that the direct evidence provided by density difference plots for electron transfer from 1-PyH⁺ to GaP(110) is confirmed by several different electron population analyses.

Musgrave and co-workers hypothesized that H₂O molecules adsorbed on Ga surface sites might prevent 1-PyH⁺ from transferring an electron back to the surface, as the empty Ga orbitals are already occupied by the H₂O oxygen lone pair and cannot host an extra electron from 1-PyH⁺.³¹ 1-PyH⁺ therefore might be stable when in contact with the solvated GaP(110) surface, in contrast to what was just concluded above. To test this hypothesis, we compare the electron density difference plot for 1-PyH⁺ adsorbed on the bare GaP(110) periodic slab to the one for 1-PyH⁺ adsorbed on the explicitly solvated GaP(110) periodic slab (Figure 6.3). The explicitly solvated GaP(110) surface was modeled as described in section 6.2.1. While we still observe a net decrease of electron density surrounding 1-PyH⁺ when adsorbed water is present on the surface, this effect is less pronounced compared to what was observed using a bare slab model. Bader charge analysis confirms this finding, yielding a net transfer of 0.18 e negative charge from 1-PyH⁺ to the GaP surface and surrounding water layer (compared to 0.45 e observed on the bare slab). For the explicitly solvated slab, the increase in electron density is mostly confined to the water layer and the region in between the water layer and the 1-PyH⁺ radical; however, we observe a similar increase in electron density localized on a Ga surface atom in the case of both the explicitly solvated slab and the bare slab. Overall, we can conclude that water adsorption on the GaP(110) surface does reduce the ability of 1-PyH⁺ to transfer an electron to the surface;
nevertheless, we still observe a transfer of electron density which might suggest that 1-PyH• is unstable.

Figure 6.3 Electron density difference plot of the 1-pyridinyl radical (1-PyH•) on top of (a) the bare GaP(110) surface simulated with a periodic slab model and (b) the GaP(110) surface with an adsorbed monolayer of half-dissociated water molecules simulated with a periodic slab model. Ga atoms are depicted in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in white. Increases in electron density are depicted in yellow, while decreases are depicted in blue. Isosurface level = 0.001 e/bohr³. Figure 6.3a is a reproduction of Figure 6.1b, which is reproduced here for the reader’s convenience. Figure adapted from Ref. 32. Copyright 2016 American Chemical Society.

Musgrave and co-workers have also suggested that the negative bias applied to the electrode will lead to the occupation of all surface Ga states, therefore preventing the back-transfer of an electron from the 1-PyH• radical.³¹ We note that the surface electron density required to occupy all such states would be on the order of ~8-10 e⁻ nm⁻² (i.e., 2 e⁻ per surface Ga
atom, 4 surface Ga atoms per 0.78 nm × 1.17 nm unit-cell). Experimental measurements of surface electron density on GaP are unavailable to our knowledge. However, Durrant and co-workers measured maximum surface charge carrier densities of ~2-3 h⁺ nm⁻² on a related hematite photo-electrode.⁴⁻³ We would need to add approximately ~1-2 additional electrons to our cluster model of the GaP(110) surface to achieve a similar carrier density on our GaP(110) cluster model, as was done in Chapters 4 and 5 to model the photoelectrode negative charge. We thus conclude that the negative bias will not lead to the occupation of all surface Ga states.

### 6.3.2 GaP(110) Band Edge Positions

Next, we sought to verify whether the result of the electron density difference and Bader charge analyses is consistent with the reducing power of the photoexcited electrons produced at a GaP photocathode, with respect to PyH⁺ reduction to 1-PyH⁺. For this purpose, we first need to compute the position of the GaP(110) CBₘᵢₙ, which, as discussed in section 6.2.1, requires the computation of both the band gap and the BGC.

<table>
<thead>
<tr>
<th>Type of transition</th>
<th>GaP band gap (eV)</th>
<th>GaP band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Computed</td>
<td>Experimental</td>
</tr>
<tr>
<td>Indirect</td>
<td>2.47</td>
<td>2.22</td>
</tr>
<tr>
<td>Direct</td>
<td>2.62</td>
<td>2.78</td>
</tr>
</tbody>
</table>

Table 6.2 Comparison of computed and experimental⁴⁻³⁴ GaP band gap values. Table adapted from Ref. 25. Copyright 2015 American Chemical Society.

We report our results of direct and indirect band gap from G₀W₀ calculations and we compare them to experimental values in Table 6.2. Our computed values and the experimental
values are in good agreement. The comparison between our calculated band gap from $G_0 W_0$ calculations (2.47 eV) and the experimental value (2.22 eV) suggests that the uncertainty in the computed band edge positions is $\sim 0.1$ eV because the computation of these values requires the half band gap rather than the band gap. The half band gap is used to derive the energy shift of the band edges with respect to the BGC (see Ref. 26 for more details).

<table>
<thead>
<tr>
<th>Band edge</th>
<th>Bare slab</th>
<th>Explicitly solvated slab</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CB_{\text{min}}$</td>
<td>-3.57 eV</td>
<td>-2.77 eV</td>
</tr>
<tr>
<td>$VB_{\text{max}}$</td>
<td>-6.04 eV</td>
<td>-5.24 eV</td>
</tr>
</tbody>
</table>

Table 6.3. Position of the GaP(110) conduction band minimum ($CB_{\text{min}}$) and valence band maximum ($VB_{\text{max}}$) computed with and without an explicit layer of water molecules adsorbed on the surface of the GaP(110) periodic slab model.

In an aqueous environment, the GaP(110) surface will be covered with adsorbed water molecules that could alter the $CB_{\text{min}}$, as Musgrave and co-workers pointed out. Therefore, we derived the BGC from the work function of the GaP(110) surface computed both in the absence and presence of adsorbed explicit water molecules. We found that the computed work function of the solvated GaP(110) slab is 0.8 eV lower in energy than the computed work function of the same slab in vacuum (4.8 eV). This is an expected result, as water adsorption typically causes a decrease of the work function due to the polarity of the H$_2$O molecule and of its bond with the surface. The more accurate work function of the solvated surface, coupled with the computed GaP band gap, was then used to determine the $CB_{\text{min}}$ position in the presence of solvating water molecules. We compare the $CB_{\text{min}}$ and the valence band maximum ($VB_{\text{max}}$) computed with the bare slab and the explicitly solvated slab in Table 6.3. The $CB_{\text{min}}$ position is
shifted to -2.77 eV vs. vacuum, given the decrease in work function caused by water adsorption. This indicates a greater reducing power of photoexcited electrons generated from the GaP electrode in the presence of the aqueous environment.

Note that the band edges of any semiconductor are affected by the pH of the solution in contact with the semiconductor surface, as the pH will determine the nature of the charged adsorbates (H+, OH-) that will in turn shift the band edges. The calculated band edge positions reported in Table 6.3 can be considered to be at the pH of zero charge (pH\text{ZC}), given that our calculations were performed with a neutral surface in vacuum. We were not able to find experimental data for pH\text{ZC} of GaP but pH\text{ZC}=7 is usually considered a good estimate as it corresponds to neutrality of the aqueous solution in contact with the electrode. Given this value, we can then shift the computed band edge positions according to the desired pH (e.g., experimental pH=5.2) using the following equation:\textsuperscript{26}

$$E(VB_{max}/CB_{min})(pH) = E(VB_{max}/CB_{min})(pH_{ZC}) + 0.059 \cdot (pH - pH_{ZC}) \quad (6.6)$$

The resulting CB\text{min} at the experimental pH (5.2) and derived from the more accurate work function computed with explicit solvation is -2.87 eV relative to the vacuum level and -1.66 V vs. SCE. This value is employed in the following for comparison to the reduction potentials of various PyH\textsuperscript+ reduction reactions. While the CB\text{min} position is affected by pH, reduction potentials are not affected by pH unless the reduction process involves protonation of the reactant.

Finally, note that the CB\text{min} position will likely not be affected by the small cathodic potential applied in the Bocarsly experiments. The applied potential typically serves to move the Fermi level of the metal counter electrode below the potential for the water oxidation reaction\textsuperscript{36}
and, for the scenario where the band edges are not pinned,\textsuperscript{37} could provide additional reducing potential for the photoexcited electrons in p-GaP. However, in the ideal (defect-free) case, the band edges are pinned at the solution-semiconductor interface and the applied potential only affects the magnitude and the direction of the band bending.\textsuperscript{36,37} In the Bocarsly experiments, the negative applied potential may therefore increase the downward bending of the band edges and enhance electron-hole separation at the solution-semiconductor interface, but it likely does not shift the CB\textsubscript{min} in a favorable direction to increase electron transfer to PyH\textsuperscript{+}.

6.3.3 Comparison of GaP(110) Conduction Band Minimum to Reduction Potentials Associated with Pyridinium Reduction Pathways

We will now compare the computed CB\textsubscript{min} of solvated GaP(110) to the one-electron reduction potential for PyH\textsuperscript{+}\textsubscript{sol}→1-PyH\textsuperscript{•}\textsubscript{sol} to establish whether or not this reaction can occur, based on the reducing power of the photoexcited electrons from the p-GaP electrode (Figure 6.4). We find that the CB\textsubscript{min} of solvated GaP(110) is higher in energy (by ~0.2 eV) than the one-electron reduction potential for PyH\textsuperscript{+} reduction to 1-PyH\textsuperscript{•}. This suggests that 1-PyH\textsuperscript{•} might form under experimental conditions, as hypothesized by Musgrave and co-workers.\textsuperscript{7,31} This process, however, is nearly thermoneutral, and we cannot definitively conclude whether it is thermodynamically feasible when considering the uncertainty related to both the computed CB\textsubscript{min} (~0.1 eV, \textit{vide supra}) and the computed reduction potential (~0.3 eV, Ref. 9 and references therein).
Figure 6.4 Comparison of computed relevant energies, relative to the vacuum level (values reported in black), and relevant potentials, relative to the saturated calomel electrode (SCE) (values reported in blue): GaP(110) conduction band minimum (CB$_{\text{min}}$) computed with non-self-consistent GW ($G_0W_0$) calculations and explicit solvation at pH=5.2 (CB$_{\text{min-GW-solv}}$, red dashed line) and reduction potential values ($E^0$) for different solvated pyridinium (PyH$^+$$_{\text{sol}}$) reduction pathways (black rectangles). These pathways are: reduction to the solvated 1-pyridinyl radical (PyH$^+$$_{\text{sol}}$$\rightarrow$1-PyH•$_{\text{sol}}$) and reduction to adsorbed pyridine (Py) and an adsorbed hydrogen atom (PyH$^+$$_{\text{sol}}$$\rightarrow$Py*$_{\text{ads}}$+H*). * indicates adsorbed species and the subscript “sol” indicates species in solution. $E^0$ PyH$^+$$_{\text{sol}}$$\rightarrow$1-PyH•$_{\text{sol}}$ is taken from Ref. 9. Values on the vacuum scale were converted to the SCE scale and vice versa by using the absolute value of the standard hydrogen electrode (SHE) -4.281 V$^{29}$ converted to the SCE value -4.525 V (see section 6.2.2 for more details).

The reduction potential for PyH$^+$ reduction to 1-PyH$^*$ ($E^0$ PyH$^+$$_{\text{sol}}$$\rightarrow$1-PyH$^*$$_{\text{sol}}$) reported in Figure 6.4 is for a homogeneous process. Adsorption of PyH$^+$ on the GaP surface could catalyze
the reduction of this species to 1-PyH\(^{\star}\), thus decreasing its reduction potential as previously proposed on Pt(111).\(^{10}\) In Chapter 4, we used our GaP(110) solvated cluster model to investigate the adsorption of several species including PyH\(^{\star}\). In that study, we also added extra electrons to the solvated cluster model to simulate the negative charge of the photoelectrode. Modeling this aspect can be especially important for PyH\(^{\star}\) because electrostatic attraction could likely be the key to a more favorable adsorption for a positively charged species. However, we found that PyH\(^{\star}\) adsorption is not favored even when the surface is negatively charged. We conclude that PyH\(^{\star}\) reduction to 1-PyH\(^{\star}\) cannot be catalyzed by adsorption on the surface and adsorbed PyH\(^{\star}\) cannot play a role in CO\(_2\) reduction catalysis.

Next, we investigate alternative PyH\(^{\star}\) reduction pathways given that our results above suggest that there is a low thermodynamic driving for reducing PyH\(^{\star}\) to 1-PyH\(^{\star}\).and yet experiments suggest that PyH\(^{\star}\) is essential to the catalysis. Specifically, we study possible heterogeneous reduction mechanisms (Figure 6.5) using our implicitly solvated cluster model. We started by investigating a reduction mechanism analogous to the one proposed by Batista and co-workers on Pt(111).\(^{11}\) In this reduction mechanism, solvated PyH\(^{\star}\) undergoes a one-electron reduction to an adsorbed hydrogen atom and solvated Py (PyH\(^{\star}\)\(_{\text{sol}}\rightarrow\text{Py}_{\text{sol}}^{\star}+\text{H}^{\star}\)). While this mechanism was computationally found to have a moderate reduction potential on Pt(111) (-0.72 V vs. SCE), we found that this mechanism will require a -1.41 V vs. SCE applied potential to occur on GaP(110). However, if Py adsorbed next to the adsorbed hydrogen atom was modeled as a product (PyH\(^{\star}\)\(_{\text{sol}}\rightarrow\text{Py}^{\star}+\text{H}^{\star}\)) instead of solvated Py, we found a much lower reduction potential (-0.85 V vs. SCE).
Figure 6.5 Alternative pathways for pyridinium (PyH⁺) reduction on the GaP(110) surface: one-electron reduction to pyridine (Py) in solution and adsorbed hydrogen atom (PyH⁺ₚₒˡ→Pyₚₒˡ+H*) and to adsorbed Py and adsorbed hydrogen atom (PyH⁺ₚₒˡ→Py⁺ₚₒˡ+H*). Reduction potential values are expressed in V versus saturated calomel electrode (SCE). Ga atoms are represented in blue, P atoms in green, C atoms in violet, N atoms in light blue, and H atoms in white. * indicates adsorbed species and the subscript “sol” indicates species in solution. Note that PyH⁺ₚₒˡ→Pyₚₒˡ+H* is a reduction pathway analogous to the one proposed by Batista and co-workers on Pt(111).¹¹

In Figure 6.4, we compare the one-electron reduction potential for PyH⁺ₚₒˡ→Py⁺ₚₒˡ+H* to the one-electron reduction potential for PyH⁺ₚₒˡ→1-PyH⁺ₚₒˡ and to the position of GaP(110) CBₘᵢₙ computed with accurate G₀W₀ calculations. This comparison suggests that PyH⁺ₚₒˡ→Py⁺ₚₙ+H* reduction is much more likely to occur by transfer of photoexcited electrons than the previously discussed PyH⁺ₚₒˡ→1-PyH⁺ₚₒˡ reduction, since CBₘᵢₙ lies higher in energy than the reduction potential for PyH⁺ₚₒˡ→Py⁺ₚₙ+H* by ~0.8 eV while it lies higher in energy than the reduction potential for PyH⁺ₚₒˡ→1-PyH⁺ₚₒˡ by only ~0.2 eV. Furthermore, the barrier is expected to be much higher for PyH⁺ₚₒˡ→1-PyH⁺ₚₒˡ than for PyH⁺ₚₒˡ→Py⁺ₚₙ+H* based on the
difference in exoergicity between these two possible reduction pathways (~0.6 eV). We therefore conclude that \( \text{PyH}^+_{\text{sol}} \rightarrow \text{Py}^* + \text{H}^* \) is likely the preferred \( \text{PyH}^+ \) reduction pathway. This result is crucial in the context of the heterogeneous mechanism on GaP(110) proposed by Keith and Carter.\(^{13,14}\) In fact, in this mechanism, adsorbed Py and adsorbed hydride-like species are the reactants needed for the formation of the active catalyst adsorbed DHP.\(^{38}\) Therefore, \( \text{PyH}^+ \) could contribute to the active catalyst formation by being reduced to adsorbed hydrogen and adsorbed Py.

6.3.4 Comparison Between GaP(111) and GaP(110) Properties\(^{\S\S}\)

Recent experiments by Hu and Bocarsly\(^{15}\) show that the GaP(110) facet yields higher current densities than the GaP(111) facet under the \( \text{CO}_2 \) reduction conditions employed in their original study.\(^2\) Our group computed the \( \text{CB}_{\text{min}} \) of solvated GaP(111) in a separate study,\(^{39}\) and here we compare it to the \( \text{CB}_{\text{min}} \) of solvated GaP(110) (Figure 6.6). The \( \text{CB}_{\text{min}} \) of the GaP(111) and GaP(110) surfaces are only separated by 0.08 eV. Both surfaces thus should provide a similar thermodynamic driving force to induce any homogeneous reduction step, provided that such a reduction is not affected by any interaction with the surface other than receiving a photoexcited electron. Therefore, the observed varying electrochemical performances between the two surfaces must be attributed to a difference in the way intermediates interact with the surface, which in turn affects the rate of elementary steps occurring in a heterogeneous mechanism. We therefore conclude that a homogeneous mechanism such as the one suggested by Musgrave and co-workers\(^7\) (\(i.e.,\) a mechanism requiring \( \text{PyH}^+_{\text{sol}} \rightarrow 1-\text{PyH}^*_{\text{sol}} \)) is likely not the primary pathway for \( \text{CO}_2 \) reduction in this system. In contrast, a heterogeneous mechanism in which the active

\(^\S\S\) The results for the GaP(111) surface were provided by Dr. Thomas P. Senftle, who is currently a postdoctoral research associate in our group.
catalytic sites are molecules stabilized on the surface like the one proposed by Keith and Carter\textsuperscript{13,14} better explains the observed, surface-dependent activity.

Figure 6.6 Comparison of relevant conduction band minima (CB\textsubscript{min}) (red dashed lines) and reduction potentials (black rectangles): CB\textsubscript{min} of solvated GaP(110) and GaP(111) at pH = 5.2 computed with G\textsubscript{0}W\textsubscript{0} calculations (CB\textsubscript{min-GW-solv}), reduction potential (E\textsuperscript{0}) for pyridinium (PyH\textsuperscript{+}) reduction to the solvated 1-pyridinyl radical (PyH\textsuperscript{+}\textsubscript{sol}→1-PyH\textsuperscript{•}\textsubscript{sol}), and E\textsuperscript{0} for PyH\textsuperscript{+} reduction to adsorbed pyridine (Py) and an adsorbed hydrogen atom (PyH\textsuperscript{+}\textsubscript{sol}→Py\textsuperscript{*}+H\textsuperscript{*}) on the GaP(110) and GaP(111) surfaces. * indicates adsorbed species and the subscript “sol” indicates species in solution. E\textsuperscript{0} PyH\textsuperscript{+}\textsubscript{sol}→1-PyH\textsuperscript{•}\textsubscript{sol} is taken from Ref. 9. Values on the vacuum scale (reported in black) were converted to the saturated calomel electrode (SCE) scale (values reported in blue) and vice versa by using the absolute value of the standard hydrogen electrode (SHE) -4.281 V\textsuperscript{29} converted to the SCE value -4.525 V (see section 6.2.2 for more details). Figure adapted from Ref. 32. Copyright 2016 American Chemical Society.
<table>
<thead>
<tr>
<th>Species</th>
<th>GaP(110)</th>
<th>GaP(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py</td>
<td>-9.3</td>
<td>-6.5</td>
</tr>
<tr>
<td>o-DHP</td>
<td>-8.2</td>
<td>-3.5</td>
</tr>
<tr>
<td>PyH⁺</td>
<td>+5.5</td>
<td>+6.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>+2.5</td>
<td>+5.8</td>
</tr>
<tr>
<td>H₂O</td>
<td>-2.0</td>
<td>+2.0</td>
</tr>
</tbody>
</table>

Table 6.4 Adsorption free energies at room temperature (kcal/mol) of relevant species (pyridine (Py), 1,2-(ortho)-dihydropyridine (o-DHP), pyridinium (PyH⁺), CO₂, and H₂O) on the GaP(110) and GaP(111) implicitly solvated cluster models. Data reported for GaP(110) are reproduced from Table 4.2 of Chapter 4. Table adapted from Ref. 32. Copyright 2016 American Chemical Society.

The observed difference in activity for GaP(110) and GaP(111) could be explained by different adsorption trends on the two surfaces. To test this hypothesis, we compare the adsorption strengths of different species relevant to our proposed heterogeneous mechanism on the two surfaces (Table 6.4). We report the adsorption free energies of PyH⁺, CO₂, H₂O, and Py, as they are all present under experimental conditions; furthermore, we report the adsorption free energy of the 1,2-(ortho)-dihydropyridine (o-DHP) isomer of DHP, which is a proposed catalytic intermediate in this system. As already discussed in section 4.7 of Chapter 4, only one of the two isomers of DHP is considered here for simplicity. Except for PyH⁺ adsorption, which is almost equally unfavorable on both surfaces, we find a non-negligible difference in adsorption free energy between the two surface facets. This supports the hypothesis that varying activity is attributed to a difference in interaction strengths between the surface and intermediate species.
involved in a heterogeneous mechanism. Specifically, for CO₂, H₂O, Py, and o-DHP, adsorption on GaP(110) is more favorable than adsorption on GaP(111) by at least 2.8 kcal/mol, with o-DHP exhibiting the largest difference (4.7 kcal/mol). As shown in Figure 6.6, the varying adsorption strengths result in a thermodynamic driving force for the reduction of PyH⁺ to adsorbed Py and an adsorbed hydrogen that is 0.36 V more favorable on GaP(110) compared to GaP(111), which may explain the higher activity observed over the (110) surface facet. We conclude based on the evidence presented above that the most favorable CO₂ reduction mechanism in this system must be heterogeneous. The only heterogeneous mechanism proposed so far over p-GaP photo-electrodes involves adsorbed DHP as the active catalyst.¹³,¹⁴

6.4 Conclusions

In conclusion, we confirmed that an electron cannot be stably transferred from the GaP(110) surface to PyH⁺ to form 1-PyH⁻ using accurate periodic calculations with pure and hybrid DFT theory. We also tested the effect of explicit solvation of the surface and found that water adsorption on GaP(110) does not fully prevent back electron transfer from 1-PyH⁻ to the surface. We further investigated the feasibility of 1-PyH⁻ formation via PyH⁺ reduction by comparing the CB_{min} of solvated GaP(110) computed with accurate G₀W₀ calculations to the most accurate previously computed⁹ one-electron reduction potential of PyH⁺, which also happens to be the average value of the four independently calculated values reported in the literature.⁸–¹¹ We found that the CB_{min} lies at a slightly more negative potential (~0.2 V difference) than the one-electron reduction potential for PyH⁺ reduction to 1-PyH⁻ and, given the uncertainty on these computed values, we could not conclude whether or not this process is thermodynamically feasible. PyH⁺ adsorption was previously proposed to lower its reduction potential on Pt(111);¹⁰ however, in
Chapter 4 we found that PyH\(^+\) does not adsorb on the GaP(110) surface even when simulating a negatively charged electrode surface. Finally, given that we found a small thermodynamic driving force for PyH\(^+\) reduction to 1-PyH\(^-\) and that this reaction cannot be catalyzed via PyH\(^+\) adsorption, we investigated alternative PyH\(^+\) reduction pathways. We found that reducing PyH\(^+\) to adsorbed Py and an adsorbed hydrogen atom is favored and more likely to occur than PyH\(^+\) reduction to 1-PyH\(^-\) under experimental conditions. Interestingly, this more favorable reduction pathway also leads to the generation of the reactants needed for adsorbed DHP formation, which is the active catalyst in the mechanism for CO\(_2\) reduction on p-GaP photocathodes proposed by Keith and Carter.\(^{13,14}\)

In this chapter, we also discovered significant evidence supporting the hypothesis that the mechanism of CO\(_2\) reduction in this system is heterogeneous. We found that solvated GaP(110) and GaP(111) have similar CB\(_{\text{min}}\), suggesting that photoexcited electrons from either facet can equally promote homogeneous processes. However, these two surfaces have been observed to display a different activity towards CO\(_2\) reduction,\(^{15}\) thus suggesting that the mechanism cannot be fully homogeneous and the surface must be at least partly involved. Specifically, the observed difference in activity for the two surfaces might be explained by differences in adsorption strength for relevant intermediates in the CO\(_2\) reduction mechanism.

### 6.5 References


Chapter 7

Hydride Transfer at the GaP(110)/Solution Interface: Mechanistic Implications for Pyridine-Catalyzed CO₂ Reduction

7.1 Introduction

The heterogeneous mechanism proposed by Keith and Carter for pyridine (Py)-catalyzed CO₂ reduction on p-GaP photoelectrodes¹,² presented in section 1.3.2 and illustrated in Fig. 1.3 of Chapter 1 is supported by several computational and experimental results as discussed there. This mechanism is supported further by results presented in previous chapters of this dissertation. In Chapter 3, we found that water dissociation is thermodynamically favored on the GaP(110) surface and leads to the formation of adsorbed protons on the P surface sites. In Chapter 5, we showed that these protons are very stable under experimental conditions and can potentially be reduced to surface hydrides (H*ₚ) and react with adsorbed Py to form the proposed active catalyst adsorbed dihydropyridine (DHP). In Chapter 6, we found that reducing pyridinium (PyH⁺) to adsorbed Py and an adsorbed hydrogen atom is thermodynamically favored under experimental conditions and more likely to occur than the previously proposed reduction to the 1-pyridinyl radical (1-PyH'). PyH⁺ reduction therefore might contribute to formation of the proposed active catalyst adsorbed DHP, resulting in the overall mechanism summarized in Figure 7.1. Finally, we also provided key evidence supporting the hypothesis that surface adsorbed species (e.g., Py and DHP) must play a role in the catalytic mechanism.
Although the aforementioned experimental and computational results support the heterogeneous mechanism in Figure 7.1, this mechanism is not validated fully yet. In this chapter, we use our solvated cluster models with hybrid density functional theory (DFT) to investigate the energetics of the hydride transfer (HT) steps involved in this mechanism. We will determine whether these HTs are thermodynamically viable by using computed thermodynamic hydricities ($\Delta G_{\text{hyd}s}$). Furthermore, we draw important conclusions regarding whether $\text{H}^*$s and adsorbed DHP formed via $\text{H}^*$ and aqueous proton transfer can participate in the mechanism of Py-catalyzed CO$_2$ reduction on p-GaP photo-electrodes based on computed reaction free energies ($\Delta G$s) and activation energies ($\Delta G^\ddagger$s).

7.2 Computational Approach

We performed all calculations using the same cluster model and computational details presented in section 4.2.2 of Chapter 4. The cluster model was used in this chapter to compute $\Delta G_{\text{hyd}s}$ of $\text{H}^*$s and other adsorbed species as well as to model $\text{H}^*$ transfer reactions.

We simulated species adsorption and surface reactions using our mixed solvation approach consisting of the continuum Solvation Model based on solute electron Density (SMD)$^3$ and a full monolayer of half-dissociated water molecules adsorbed on the cluster surface (section 4.4.2 of Chapter 4). We followed the same procedure described there to generate the free
adsorption sites needed here for these calculations. \( \Delta G_{\text{hyds}} \) of molecules in solution were calculated using a mixed solvation approach consisting of SMD and different numbers of explicit water molecules, depending on the species under study. For each species, we used the same number of explicit water molecules as in Chapter 5, where we calculated the acidity constant of species in solution. We refer the reader to section 5.2 of that chapter for the reasoning behind the choice of the number of explicit water molecules. We used one explicit water molecule for 1,2-(ortho)-dihydropyridine (\( o \)-DHP) and \( \text{PyH}^+ \), and we used three explicit water molecules for \( \text{HCOO}^- \) and \( \text{CO}_2 \). Note that, as we have done in previous chapters, here we will only consider one of the two possible isomers of DHP: \( o \)-DHP. A justification for this choice is provided in section 4.7 of Chapter 4. In the case of HCOOH, we did not use any explicit water molecule due to the high instability of the hydride dissociation product \( \text{COOH}^+ \). In the presence of explicit water molecules, \( \text{COOH}^+ \) will spontaneously donate its proton to a water molecule, thus forming \( \text{CO}_2 \) and \( \text{H}_3\text{O}^+ \).

We performed a frequency analysis to verify each minimum-energy structure (\textit{i.e.,} no imaginary frequency expected) and transition state (TS) structure (\textit{i.e.,} only one imaginary frequency corresponding to the correct reaction coordinate expected). TSs were optimized with the eigenvector-following method as implemented in Orca.\(^4\) We further verified the optimized TS structures by relaxing along both directions of the eigenvector corresponding to the imaginary frequency and observing that the structures thus obtained corresponded to the expected initial state (IS) and final state (FS). The computed frequencies were then used to calculate thermal corrections at room temperature (298.15 K) as described in section 4.2.2 of Chapter 4.
ΔG\textsubscript{hyd}s were computed using an approach similar to the one reported by Marjolin and Keith.\textsuperscript{5} In this approach, ΔG\textsubscript{hyd} of a species is simply defined as the reaction free energy in solution for the dissociation of a hydride from this species. Marjolin and Keith computed ΔG\textsubscript{hyd} using a thermodynamic cycle, which requires the calculation of the reaction free energy in the gas phase and the solvation energy of each species involved in the dissociation equilibrium. However, as discussed in section 5.2 of Chapter 5, recent studies have shown that, when using SMD, reaction free energies in solution can be directly computed instead of having to use the more time-consuming thermodynamic cycles (as they require more calculations) without repercussion on the accuracy of the results.\textsuperscript{6,7} The use of the direct approach was also validated in Chapter 5, where we computed the acidity constants of many species relevant to the system under study using thermodynamic cycles as well as the direct approach. We found no significant differences between the two sets of results, based on which we chose to employ the direct approach there and also in this chapter. We used the following expression to calculate ΔG\textsubscript{hyd} for a generic species XH dissociating a hydride via the reaction \text{XH\textsubscript{aq}} → \text{X\textsuperscript{+aq}} + \text{H\textsuperscript{-aq}}:

\[ ΔG_{hyd} = G_{aq}(X^+) + G_{aq}(H^-) - G_{aq}(XH) \]  \hspace{1cm} (7.1)

The solution free energies of species X\textsuperscript{+} and XH (\(G_{aq}(X^+)) and \(G_{aq}(XH)) were directly calculated by modeling X\textsuperscript{+} and XH with our computational approach. The free energy of a solvated hydride (\(G_{aq}(H^-)) was calculated using an expression similar to the one employed by Marjolin and Keith in their work:\textsuperscript{5}

\[ G_{aq}(H^-) = G_{g}(H_2) - G_{aq}(H^+) + ΔG_{aq,hetero} \]  \hspace{1cm} (7.2)
$G_{aq}(H^-)$ thus was obtained by subtracting the free energy of a solvated proton ($G_{aq}(H^+)$) and adding the energy for the heterolytic dissociation of H$_2$ in aqueous solution ($\Delta G_{aq,hetero}$) to the free energy of H$_2$ in the gas phase ($G_g(H_2)$). $G_g(H_2)$ was calculated by modeling a H$_2$ molecule in the gas phase with our computational approach given above. For $G_{aq}(H^+)$, we used the empirical value of -270.3 kcal/mol, which is given by the sum of different contributions as described in section 5.2 of Chapter 5. Finally, for $\Delta G_{aq,hetero}$, we used the value recently recommended by Appel and co-workers (34.2 kcal/mol) instead of the value employed by Marjolin and Keith (42.1 kcal/mol, which was first reported by Pearson). Note that our goal in this chapter is not to reproduce or predict experimental hydricities, but to establish relative hydride donor and acceptor abilities for a series of species relevant to the proposed mechanism. We therefore could have chosen either value of $\Delta G_{aq,hetero}$; however, we chose to use the value recently recommended by Appel and co-workers, which was accurately determined based on values derived from rigorous treatment of experimental data and using consistent standard states (i.e., 1 atm for gases and 1 M for species in solution).

By implementing this approach for $\Delta G_{hyd}$ calculations and the value of $\Delta G_{aq,hetero}$ recommended by Appel and co-workers, $\Delta G_{hyd}$ of HCOO$^-$ in aqueous solution was found to be equal to 28.4 kcal/mol when using only implicit solvation and 30.6 kcal/mol when using a mixed implicit-explicit solvation approach. These values are qualitatively consistent with the value derived from experimental data by Appel and co-workers (24.1 kcal/mol). Based on our definition of $\Delta G_{hyd}$, the increase in the computed $\Delta G_{hyd}$ of HCOO$^-$ in solution when including explicit water molecules suggests that the dissociation of a hydride and formation of CO$_2$ is less favored under this condition. This observation can be readily explained when considering that
HCOO\(^{-}\), a negatively charged and polar molecule, interacts more strongly than CO\(_2\) does with the solvating water molecules.

The \(\Delta G_s\) and \(\Delta G^\#\)s were computed using a “super-molecule (SM) approach” in which the energy of the IS for a certain reaction is calculated by simulating all reactant species in the same calculation in contact with each other. This approach has the advantage in that the IS and FS are well connected to the TS, thus allowing a more rigorous calculation of reaction energetics. However, we have to neglect rotational and translational contributions to the free energy of non-adsorbed reactants (e.g., PyH\(^+\) and CO\(_2\)) when using this approach. We thus also tested a “separate reactants (SR) approach” in which the energy of each individual reactant species is calculated in a separate calculation. Therefore, while the IS is no longer well connected to the TS, the rotational and translational contributions to the free energy of the non-adsorbed reactants are included in the overall IS free energy. We found that the two approaches gave reasonably similar results, with \(\Delta G\) and \(\Delta G^\#\) differences of \(~4\) kcal/mol at most. The two approaches and their comparison are discussed further in section 7.3.2.

### 7.2.1 Global Optimization and Computation of Two-Dimensional Potential Energy Surfaces

In section 7.3.2.1, we use two-dimensional potential energy surfaces (PESs) to study the energetics of adsorbed o-DHP formation via H\(^+\)\(_{\text{sol}}\) transfer and H\(^+\) transfer to adsorbed Py. H\(^+\)\(_{\text{sol}}\) was modeled as an Eigen cation (i.e., H\(_3\)O\(^+\) solvated by three H\(_2\)O molecules) based on our pK\(_a\) results presented in Chapter 5, showing that this model correctly captures the acidity of a proton in solution within our computational approach. The structure used as a starting point to generate these PESs (Figure 7.7 and Figure 7.8 in section 7.3.2.1) was obtained with an extension of the OGOLEM code\(^{11}\) via the following steps:
a) Place the optimized Eigen cation structure above the fully relaxed, explicitly solvated cluster surface with one adsorbed H$_2$O replaced by adsorbed Py and two extra electrons added to the system in order to model H$^*$, as dictated by microscopic reversibility. Note that the addition of the two extra electrons causes a surface Ga atom to rise out of plane, which in turn causes one adsorbed H$_2$O molecule to desorb (Figure 7.2).

b) Perform a grid-based search over Cartesian translations and Euler rotations of the Eigen cation with respect to the cluster surface around a point representing a good starting guess for the center of mass of the Eigen cation (increments used: 0.1 Ångstrom (Å), 30 degrees). More specifically, the center of mass of the Eigen cation was placed -0.463/3.667/3.0333 (x/y/z) Å away from the nitrogen atom of adsorbed Py. This point is represented by the orange sphere in Figure 7.3.

Step b yielded 329 structures as initial guesses for subsequent local optimizations.

Figure 7.2 (a) Side and (b) top views of the reactant structure obtained from global optimization. Note one of the surface Ga atoms rising out of plane due to the addition of the two extra electrons. This causes one adsorbed H$_2$O to desorb. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.
Figure 7.3 Structure illustrating the input center of mass of the Eigen cation represented by the orange sphere. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.

c) Loosely optimize each structure from step b while keeping the entire GaP cluster and the adsorbed water molecules not directly interacting with the Eigen cation frozen in place.
d) Select the 20 most stable structures from step c and fully relax them (as always, we kept all capping H atoms on the cluster frozen in place).
e) Select the five most stable structures among the fully relaxed structures and perform a vibrational frequency analysis for each of them.

Step e revealed that only three structures were true minima and almost isoenergetic (0.8 kcal/mol differences in energy). However, the Eigen cation was lost in these structures as one of the surface OH⁻ got protonated. We therefore continued with the following steps:

f) Protonate the two adsorbed OH⁻ and regenerate the Eigen cation in the 20 most stable structures from step c, then reoptimize these structures.
g) Select the five most stable structures among the fully relaxed structures and perform a vibrational frequency analysis for each of them.
Step g revealed that these five structures were almost isoenergetic (0.2-1.2 kcal/mol differences in energy), but only one was a true minimum. This structure is illustrated in Figure 7.2. Note that we removed two adsorbed H$_2$O to obtain the actual structure used for computation of the PESs (Figure 7.4). This choice was made to reduce the computational cost and facilitate the search for true minima when calculating the PES. The two adsorbed H$_2$O removed are those adsorbing on the two Ga surface sites adjacent to the Ga atom rising out-of-plane. We do not expect the removal of these adsorbed H$_2$O to affect the energetics of the reaction given that they are not directly interacting with either the Eigen cation, adsorbed Py, or H$^\circ$. This was confirmed by the close agreement between $\Delta G$ computed with (-27.2 kcal/mol) and without (-27.6 kcal/mol) these two adsorbed H$_2$O.

![Figure 7.4 (a) Side and (b) top views of the reactant structure used to compute the potential energy surfaces (PESs) illustrated in Figure 7.7 and Figure 7.8 in section 7.3.2.1. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.](image)

To calculate the PESs, we started with the reactant structure obtained using the global optimization approach. We then followed these steps:
a) We first performed a relaxed-surface scan (i.e., a series of constrained optimizations with loose convergence criteria (LooseOPT keyword in Orca) in which a certain bond length is scanned while all the other variables are allowed to relax) of the C-H bond length corresponding to the C-H bond formed when the H* is transferred to the C atom of adsorbed Py. The bond length was scanned from the equilibrium length in the globally optimized reactant to 1.1 Å, which is the equilibrium bond length of the C-H bond in the product adsorbed o-DHP.

b) For each geometry identified with the previous relaxed surface scan, we performed a relaxed surface scan of the N-H bond length corresponding to the N-H bond formed when a proton from the Eigen cation is transferred to the N atom of adsorbed Py. In this case, the scan was also performed from the equilibrium bond length identified in the previous step to 1.0 Å, which is the equilibrium bond length for the N-H bond in the product adsorbed o-DHP*.

c) We collected the energies of all structures identified with the relaxed surface scans performed in the previous steps, subtracting the reactant energy from them. We then plotted the values thus obtained as a function of the C-H and N-H bond lengths scanned with the relaxed surface scans.

7.3 Results and Discussion

7.3.1 Mechanistic Insights From Computed Thermodynamic Hydricities

In this section, we assess whether the hypothesized HTs in the heterogeneous mechanism of Figure 7.1 are thermodynamically feasible by comparing computed $\Delta G_{\text{hyd}}$s of relevant species. $\Delta G_{\text{hyd}}$ is a quantitative measure of the thermodynamic driving force for a certain species to...
dissociate a hydride: the lower $\Delta G_{\text{hyd}}$, the higher the driving force to dissociate a hydride. Relative $\Delta G_{\text{hyd}}$s therefore can be used to investigate many important mechanistic aspects. First, they can reveal whether it would be thermodynamically feasible for a certain species to donate a hydride to another species. Second, for reaction steps involving both hydride and proton transfers, they can help us understand whether the hydride and proton transfers are likely to occur concertedly or sequentially and, if sequentially, in what order. Third, $\Delta G_{\text{hyd}}$s can be used to study how the hydride donor/acceptor ability of a certain species is affected by phenomena such as surface adsorption. In the following, $\Delta G_{\text{hyd}}$s are used to investigate all of these aspects for the two HTs hypothesized in the proposed mechanism in Figure 7.1.

In the first HT, H$^*$ is transferred to adsorbed Py along with H$^+$$_{\text{sol}}$, resulting in adsorbed o-DHP formation. We can assess the feasibility of this first HT by comparing H$^*$ $\Delta G_{\text{hyd}}$ and adsorbed o-DHP $\Delta G_{\text{hyd}}$. However, such a comparison is only useful to determine whether adsorbed o-DHP can favorably form either \textit{via} a concerted proton-coupled hydride transfer (PCHT) or with H$^+$$_{\text{sol}}$ transfer first followed by H$^*$ transfer. We also computed $\Delta G_{\text{hyd}}$ of adsorbed, deprotonated 1,2-(ortho)-dihydropyridine (2-PyH$^-$) to explore the possibility of adsorbed o-DHP forming \textit{via} H$^*$ transfer first followed by H$^+$$_{\text{sol}}$ transfer. Finally, we computed $\Delta G_{\text{hyd}}$ of o-DHP in solution in order to answer a question raised by Musgrave and co-workers, which is important for the feasibility of this proposed heterogeneous mechanism: does adsorption of o-DHP cause its hydride donor ability to decrease in such a way that it can no longer transfer a hydride to CO$_2$? The second HT is from adsorbed o-DHP to CO$_2$ and leads to either HCOO$^-$ or HCOOH formation depending on the pH at the interface; if the pH at the interface is lower (higher) than HCOOH pK$_a$, then HCOOH (HCOO$^-$) will form. We also computed $\Delta G_{\text{hyd}}$ of both HCOOH and HCOO$^-$ since the exact pH at the interface is unknown.
HCOO\(^{-}\) favorably adsorbs on the GaP(110) surface, while HCOOH adsorption is thermoneutral.\(^{13}\) Thus, \(\Delta G_{\text{hyd}}\) of adsorbed HCOO\(^{-}\), adsorbed HCOOH, and HCOOH in solution were calculated. \(\Delta G_{\text{hyd}}\) of HCOO\(^{-}\) in solution was calculated for comparison to experiments (section 7.2).

We first computed H\(^{+}\) \(\Delta G_{\text{hyd}}\) by developing a physically sensible model for H\(^{+}\). We established previously that dissociative adsorption of water on GaP(110) leads to proton adsorption on P surface sites (Chapter 3 and Ref. 14); the resulting adsorbed protons have hydridic character as they draw electron density away from the P lone pairs.\(^{15}\) These results suggest that the main source of adsorbed hydrogen at the GaP(110)/H\(_2\)O interface is from heterolytically dissociated water. We expect the applied negative bias and the photoexcited electrons generated under illumination allow for further negative charging of these adsorbed protons. By contrast, the other adsorbed species formed as a result of water dissociation and adsorption (\(i.e.,\) OH\(^{-}\) and H\(_2\)O) are closed-shell and will not accept further negative charge. Thus, adsorbed protons might take on sufficient negative charge to become hydridic. Given the potential variable charge of these adsorbed protons, it is important to consider the full range of possible reactivity, namely both acidity and hydricity. In Chapter 5, we computed their acidity and found that it is very low under typical experimental conditions.\(^{13}\) These results motivated investigation of their hydricity in this chapter.

Based on the principle of microscopic reversibility, a proton and two electrons (\(i.e.,\) a hydride) must be added to our cluster model in order to simulate the reactant of a H\(^{+}\) dissociation reaction. We also include explicit solvation of the surface to improve representation of the semiconductor-water interface (see section 7.2 for more details on this solvation
Because the half-dissociated water adlayer already contains adsorbed protons, we only need to add two electrons to create the conditions for an adsorbed hydride to form. In Chapter 5, we found that explicit solvation of the surface strongly increases the stability of the adsorbed protons; a similar effect might be observed for H* s. We also tested the effect of adding a variable number of extra electrons to the system to “charge” H*. The effect of the surface solvation approach (implicit versus mixed implicit-explicit) and the effect of adding extra electrons (zero, one, and two) to the system on the computed $\Delta G_{\text{hyd}}$ are summarized in Figure 7.5. The addition of extra electrons causes a large decrease of $\Delta G_{\text{hyd}}$ (40 kcal/mol decrease when one electron is added and ~75 kcal/mol decrease when two electrons are added with the mixed solvation approach), meaning that H* dissociation becomes much more favorable under these conditions. Such a result is expected, because H* dissociation requires not only an adsorbed proton but also two electrons to dissociate from the surface and any number of electrons less than that would require ionization of the lattice to allow a hydride ion to dissociate. Explicit solvation also causes $\Delta G_{\text{hyd}}$ to decrease (~12 kcal/mol decrease when no extra electrons are added to the system) due to the extra electron density donated into the surface by adsorbed H$_2$O* and adsorbed OH-: However, explicit solvation no longer has an effect once extra electrons are added to the system, because the former does not provide as much additional electron density as added extra electrons do. Overall, we see that H* $\Delta G_{\text{hyd}}$ calculated with the mixed solvation approach and two extra electrons added to the system (1.3 kcal/mol) is appropriate for comparison to other computed $\Delta G_{\text{hyd}}$. We believe that this is a better representation of H* as the aqueous environment is properly modeled and microscopic reversibility demands two additional electrons and an adsorbed proton (provided by heterolytically dissociated water) in the model of a hydride.
To further validate our modeling choice for H\textsuperscript{+}, we computed the reduction potentials of the solvated cluster model (Table 7.1). While we recognize that the cluster model does not precisely describe the electronic structure of a periodic crystal, we can still compare the reduction potentials in Table 7.1 to GaP conduction band minimum (CB\textsubscript{min}) to qualitatively determine whether the formation of H\textsuperscript{+}\textsubscript{s} might occur on the GaP electrode under illumination. For this purpose, we use GaP(110) CB\textsubscript{min} computed in Chapter 6 using accurate non-self-consistent GW (G\textsubscript{0}W\textsubscript{0}) calculations and explicit solvation of the periodic slab to compute the work function (CB\textsubscript{min} = -1.66 V vs. saturated calomel electrode (SCE)). When computing such reduction potentials, we tested two different Ga surface sites as the localization site for the added electrons. These sites are illustrated in Figure 7.6. We observe that all computed reduction
potentials in Table 7.1 (no matter the extra electron localization site) are less negative than the computed GaP(110) CB$_{\text{min}}$, except for the first one-electron reduction potential computed localizing the added electron on a Ga site occupied by an adsorbed H$_2$O molecule (Figure 7.6b). The addition of the first electron to this site is more unfavorable because it forces a H$_2$O molecule to desorb. The most important result is that the two-electron reduction potentials computed considering either electron localization site are less negative than GaP(110) CB$_{\text{min}}$. This result suggests that these reduction reactions are likely accessible to the photoexcited electrons, and the postulated H$^*$s can form.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E$^0$ (V vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Electron localization site 1</td>
</tr>
<tr>
<td>Cluster$^+$+1e$^-$→ Cluster$^-$</td>
<td>-1.45</td>
</tr>
<tr>
<td>Cluster$^-$+1e$^-$→ Cluster$^{2-}$</td>
<td>-1.32</td>
</tr>
<tr>
<td>Cluster$^+$+2e$^-$→ Cluster$^{2-}$</td>
<td>-1.38</td>
</tr>
</tbody>
</table>

Table 7.1 Computed reduction potentials (E$^0$) for the one-electron first reduction, one-electron second reduction, and two-electron reduction of the GaP(110) cluster model solvated with our mixed implicit-explicit solvation approach. Reduction potentials are reported relative to the saturated calomel electrode (SCE). Two possible Ga surface sites were considered as the localization site for the added electrons: 1) an empty Ga surface site at the edge of the cluster (electron localization site 1, illustrated in Figure 7.6a); and 2) a Ga surface site serving as an adsorption site for one of the explicit H$_2$O molecules included in our model (electron localization site 2, illustrated in Figure 7.6b).
Next, we compare $H^* \Delta G_{\text{hyd}}$ to adsorbed $\sigma$-DHP $\Delta G_{\text{hyd}}$ and adsorbed 2-PyH$^+$ $\Delta G_{\text{hyd}}$ to investigate the mechanism of adsorbed $\sigma$-DHP formation via $H^*$ transfer. Note that PyH$^+$, which does not favorably adsorb on the surface, is formed when $\sigma$-DHP* dissociates a hydride. We therefore tested two approaches for computing adsorbed $\sigma$-DHP $\Delta G_{\text{hyd}}$: a “SM approach,” in which PyH$^+$ is modeled in contact with the GaP cluster, and a “separate products approach,” in which the free energies of PyH$^+$ and the explicitly solvated GaP cluster are computed in two separate calculations. The two approaches give similar results for adsorbed $\sigma$-DHP $\Delta G_{\text{hyd}}$ (2.4 kcal/mol difference). These results and other computed $\Delta G_{\text{hyd}}$s discussed in the following are summarized in Table 7.2.
<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G_{\text{hyd}}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-PyH-*</td>
<td>-0.5</td>
</tr>
<tr>
<td>Surface hydride</td>
<td>1.3</td>
</tr>
<tr>
<td>$\sigma$-DHP$_{\text{sol}}$</td>
<td>9.6</td>
</tr>
<tr>
<td>$\sigma$-DHP*</td>
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</tr>
<tr>
<td>HCOO$^-$_sol</td>
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</tr>
<tr>
<td>HCOO$^{-*}$</td>
<td>43.8$^a$, 39.5$^b$</td>
</tr>
<tr>
<td>HCOOH$^*$</td>
<td>46.6</td>
</tr>
<tr>
<td>HCOOH$_{\text{sol}}$</td>
<td>89.4</td>
</tr>
</tbody>
</table>

Table 7.2 Computed thermodynamic hydricities ($\Delta G_{\text{hyd}}$) in kcal/mol of relevant species based on the proposed mechanism reported in Figure 7.1: adsorbed deprotonated 1,2-(ortho)-dihydropyridine (2-PyH$^-$), surface hydride (H$^-$*), 1,2-(ortho)-dihydropyridine ($\sigma$-DHP) in solution, adsorbed $\sigma$-DHP, HCOO$^-$ in solution, adsorbed HCOO$^-*$, adsorbed HCOOH, and HCOOH in solution. * indicates adsorbed species. Subscript “sol” indicates species in solution. $^a$ Value computed using “super-molecule (SM) approach”. $^b$ Value computed using “separate products approach”. All $\Delta G_{\text{hyd}}$ values were computed with the mixed solvation approach except for HCOOH$_{\text{sol}}$ $\Delta G_{\text{hyd}}$, which was computed with the implicit solvation approach.

Adsorbed 2-PyH$^-$ $\Delta G_{\text{hyd}}$ is very similar to H$^-$* $\Delta G_{\text{hyd}}$ (1.8 kcal/mol difference) and is more than 20 kcal/mol lower than adsorbed $\sigma$-DHP $\Delta G_{\text{hyd}}$. These results suggest that there is no thermodynamic driving force to form adsorbed 2-PyH$^-$* via H$^-$* transfer to adsorbed Py and that (unsurprisingly) PyH$^+$ in solution is a much stronger hydride acceptor than adsorbed Py.
Adsorbed o-DHP therefore is more likely to form via H* transfer to PyH+ in solution or via a concerted PCHT to adsorbed Py and unlikely to form via an adsorbed 2-PyH− intermediate produced from H*. In the next section, we will consider both the reaction and the activation energies of these reaction steps to more accurately establish the most favorable pathway for adsorbed o-DHP formation via H* transfer. Adsorbed o-DHP ΔGhyd is more than 13 kcal/mol higher than o-DHP in solution ΔGhyd, showing that adsorption indeed reduces o-DHP hydride donor ability as suggested by Musgrave and co-workers. However, we need to compare adsorbed o-DHP ΔGhyd to HCOO− and HCOOH ΔGhyds to determine whether or not adsorption actually prevents o-DHP from being a good hydride donor for CO2.

If the pH at the interface is higher than HCOOH pK_a (3.8), then mostly adsorbed HCOO− is expected to form upon H* transfer to CO2. Adsorbed HCOO− ΔGhyd was computed using both the “SM approach” and “separate products approach” because the product of hydride dissociation (CO2) does not favorably adsorb on the surface. The two schemes also give similar results in this case with only ~4 kcal/mol difference. Adsorbed HCOO− ΔGhyd is relatively high (43.8 and 39.5 kcal/mol, depending on the approach), suggesting that there is a large driving force for transferring H* or a hydride from adsorbed o-DHP to CO2. Note that adsorption causes a non-negligible increase in HCOO− ΔGhyd (by 8.9 and 13.2 kcal/mol, depending on the approach) due to the large stabilization effect of adsorption on HCOO−. If the pH at the interface is lower than the HCOOH pK_a (3.8), then both HCOOH in solution and adsorbed HCOOH may form. The HCOOH ΔGhyd is much higher (by ~43 kcal/mol) in solution than when it is adsorbed due to the formation of COOH+, a very unstable species especially in solution, upon hydride dissociation. Overall, whether adsorbed HCOO−, HCOOH in solution, or adsorbed HCOOH is the CO2-reduction product, ΔGhyd for these species is much higher than ΔGhyd for all of the other
species considered in this study, thus suggesting that reduction of CO$_2$ by HT is a favorable process.

Overall, our computed $\Delta G_{\text{hyd}}$s indicate that the two HTs hypothesized in the proposed mechanism in Figure 7.1 are thermodynamically favored. Depending on the scheme used for computing adsorbed $o$-DHP $\Delta G_{\text{hyd}}$ and adsorbed HCOO$^-$ $\Delta G_{\text{hyd}}$, there is a thermodynamic driving force of at least 21.5 kcal/mol for transferring H$^*$ to adsorbed Py in a PCHT step or to PyH$^+$ in solution (thus forming adsorbed $o$-DHP) and at least 16.7 kcal/mol for transferring a hydride from adsorbed $o$-DHP to CO$_2$. Other important aspects emerge when comparing $\Delta G_{\text{hyd}}$ values. First, while $o$-DHP $\Delta G_{\text{hyd}}$ increases upon adsorption (by more than 13 kcal/mol), meaning that its hydride donor ability decreases, adsorbed $o$-DHP can still favorably donate a hydride to CO$_2$ (16.7 kcal/mol minimum driving force). Second, adsorbed 2-PyH$^-$ is clearly a better hydride donor than adsorbed $o$-DHP given its much lower $\Delta G_{\text{hyd}}$ (by at least 23.3 kcal/mol). However, the nearly equivalent adsorbed 2-PyH$^-$ $\Delta G_{\text{hyd}}$ and H$^*$ $\Delta G_{\text{hyd}}$ suggest that there exists no strong driving force to form adsorbed 2-PyH$^-$ by H$^*$ transfer to adsorbed Py. Furthermore, the p$K_a$ for adsorbed $o$-DHP (13.4) computed in Chapter 5 suggests that adsorbed 2-PyH$^-$ will likely be protonated subsequently if it forms at all. On the other hand, if adsorbed 2-PyH$^-$ could be formed via a more favorable pathway and had a long enough lifetime before being protonated, then it could potentially be a better catalyst for CO$_2$ reduction via HT than adsorbed $o$-DHP. In Chapter 8, we will investigate the thermodynamics of adsorbed 2-PyH$^-$ formation and the energetics of 2-PyH$^-$ reaction with CO$_2$. Third, given a thermodynamic driving force of at least 38.2 kcal/mol exists for transferring H$^*$ directly to CO$_2$, one could ask why adsorbed $o$-DHP would be needed to mediate this HT. The adsorption free energies computed in Chapter 4 suggest that CO$_2$ might not have access to H$^*$, because other species (such as H$_2$O, Py, and $o$-
DHP) adsorb more strongly than CO₂; under these conditions, adsorbed o-DHP might facilitate the transfer of H⁺ to CO₂. We conclude based on all of these considerations that the adsorbed DHP-mediated mechanism (Figure 7.1) cannot be excluded by our computed ΔG_{hyd}s. In the next section, we move on to investigate kinetic aspects of this mechanism.

7.3.2 Hydride Transfer Reaction Modeling

A full validation of any mechanism requires assessment of both thermodynamic and kinetic aspects. In the previous section, we used ΔG_{hyd}s to evaluate the thermodynamics of the full mechanism illustrated in Figure 7.1. We now move on to investigate the kinetics, focusing on validating two crucial hypotheses upon which this mechanism relies: that adsorbed o-DHP forms via H⁺ transfer and acts as a hydride shuttle for CO₂ reduction to HCOO⁻. The first hypothesis would be validated if ΔG⁺ for adsorbed o-DHP formation via H⁺ transfer is low enough that it can be overcome under experimental conditions. The second hypothesis (i.e., the need of adsorbed o-DHP to shuttle H⁺ from the surface to CO₂) would be strongly supported if ΔG⁺ for adsorbed o-DHP formation via H⁺ transfer was lower than ΔG⁺ for directly transferring H⁺ to CO₂. In contrast, if ΔG⁺ for adsorbed o-DHP formation via H⁺ transfer was higher than ΔG⁺ for CO₂ reduction via direct H⁺ transfer, then there would be no point in forming adsorbed o-DHP to catalyze the first step of CO₂ reduction (i.e., reduction to HCOO⁻). However, adsorbed o-DHP could still be formed and catalyze later steps of CO₂ reduction that might have higher ΔG⁺s. The thermodynamic hydricities presented in the previous section suggest that CO₂ reduction via direct H⁺ transfer is more thermodynamically favorable than adsorbed o-DHP formation via H⁺ transfer. Here, we further investigate this aspect by computing ΔG and ΔG⁺ for CO₂ reduction to adsorbed HCOO⁻ via direct H⁺ transfer and for adsorbed o-DHP formation via H⁺ transfer.
7.3.2.1 Adsorbed 1,2-(ortho)-dihydropyridine Formation via Surface Hydride Transfer

In the adsorbed DHP-mediated mechanism (Figure 7.1), we hypothesized that adsorbed o-DHP forms via H* transfer and H\textsuperscript{+}\textsubscript{sol} transfer to adsorbed Py. Our computed ΔG\textsubscript{hydr} suggest that these two transfers will either occur concertedly or sequentially with the H\textsuperscript{+}\textsubscript{sol} transfer, followed by the H* transfer. To further investigate the thermodynamic and kinetic feasibility of these hypothesized reaction steps, we computed a two-dimensional PES for adsorbed o-DHP formation via H\textsuperscript{+}\textsubscript{sol} transfer and H* transfer to adsorbed Py (Py* + H\textsuperscript{+}\textsubscript{sol} + H* → o-DHP*, Figure 7.7). H\textsuperscript{+}\textsubscript{sol} was modeled as an Eigen cation as discussed in section 7.2.1. To form the IS (Py* + H\textsuperscript{+}\textsubscript{sol} + H*), the Eigen cation was placed above the explicitly solvated cluster surface with one adsorbed water molecule removed and replaced by adsorbed Py. Replacing adsorbed H\textsubscript{2}O with adsorbed Py is justified by our adsorption free energies computed in Chapter 4, which show that Py adsorbs more strongly than H\textsubscript{2}O. Furthermore, two extra electrons were added to the explicitly solvated cluster model, which already contains an adsorbed proton, to simulate H*, as dictated by microscopic reversibility (vide supra). This is overall a rather complicated IS for which many different local minima are possible, and a normal optimization algorithm will be unlikely to find the global minimum. We thus extended the capability of the global optimization code OGOLEM\textsuperscript{16} and used it to identify the global minimum. More details of the global optimization procedure and the PES computation are provided in section 7.2.1.
Figure 7.7 Computed two-dimensional potential energy surface for adsorbed 1,2-(ortho)-dihydropyridine formation via transfer of a surface hydride and a proton directly from H₃O⁺ in solution to adsorbed pyridine (Py⁺ + H⁺ + H⁺ₘₐₜ → o-DHP*). The N-H distance corresponds to the distance between the pyridine (Py) N atom and one of the three protons belonging to H₃O⁺. The C-H distance corresponds to the distance between the Py C atom in the ortho position and the surface hydride (H⁺*). Exact N-H and C-H bond lengths that have been scanned to generate this plot are illustrated in the figure inset. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white. Reaction steps discussed in the main text are indicated by black arrows and labelled with capital letters A, B, C, D, and E.
The computed PES (Figure 7.7) was used to compare the approximate thermodynamics and kinetics of the three possible mechanisms for the reaction Py* + H⁺sol + H* → o-DHP*: a two-step mechanism with H* transfer to form an adsorbed 2-PyH⁻ intermediate followed by H⁺sol transfer (step A + step B in Figure 7.7), a concerted mechanism (step C), and a two-step mechanism with H⁺sol transfer to form a PyH⁺ in solution intermediate followed by H* transfer (step D + step E). The concerted mechanism (step C) is thermodynamically favored by more than 20 kcal/mol compared to either of the preliminary steps of the two-step mechanisms. However, step C has a higher ΔG‡ than the two-step mechanisms. Thus, we will focus on comparing the approximate energetics derived from the PES for mechanisms A+B and D+E. In fact, there is no need to consider steps B and D in our analysis. Step B is the protonation of adsorbed 2-PyH⁻ and has a very small or non-existent barrier, in agreement with the large pKₐ for o-DHP* (13.4) computed in Chapter 5. Step D is the protonation of adsorbed Py to produce PyH⁺ in solution, which is anyway present in large concentrations under experimental conditions given the solution’s acidic pH, so it does not need to be formed via this pathway; thus, the energetics of PyH⁺ formation via step D are not relevant for studying the energetics of adsorbed o-DHP formation. We therefore only compare the energetics of steps A and E. Step A is thermoneutral or only slightly thermodynamically favored; in contrast, step E is much more thermodynamically favored (by at least ~25 kcal/mol). These results are in full agreement with our computed ΔGₜₚₛ, showing that there is a much larger driving force for transferring H* to PyH⁺ in solution than to adsorbed Py. ΔGₜₚₛ for steps A and E appear to be in the same range. Thus, the kinetics of these steps will be investigated and compared in more depth in the following.
Figure 7.8 Computed two-dimensional potential energy surface for adsorbed 1,2-(ortho)-dihydropyridine formation via transfer of a surface hydride and the closest proton belonging to an Eigen cation solvating H$_2$O molecule to adsorbed pyridine (Py$^+$ + H$^*$ + H$^+_{\text{sol}}$ → $\sigma$-DHP$^*$).

The N-H distance corresponds to the distance between the pyridine (Py) N atom and the closest proton belonging to a solvating H$_2$O molecule. The C-H distance corresponds to the distance between the Py C atom in the ortho position and the surface hydride (H$^*$). Exact N-H and C-H bond lengths that have been scanned to generate this plot are illustrated in the figure inset. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.

We also computed the two-dimensional PES for transferring H$^*$ from the surface and the closest H$^+_{\text{sol}}$ belonging to a solvating H$_2$O molecule rather than H$^+_{\text{sol}}$ directly from H$_3$O$^+$ (Figure
This PES gave a very similar energy landscape to the PES in Figure 7.7, thus confirming the conclusions we have drawn above: concerted step C is the most kinetically hindered, $\Delta G^+$s for steps A and E appear to be similar, and transferring any $H^+_{\text{sol}}$ in the vicinity of adsorbed 2-PyH$^-$ is barrierless.

Step E is not only an alternative pathway for $o$-DHP* formation with respect to the one originally proposed by Keith and Carter ($Py^* + H^+_{\text{sol}} + H^* \rightarrow o$-DHP*) but it also represents a new pathway for PyH$^+$ reduction that has not been proposed so far. Thus, before computing the energetics of step E and comparing it to the energetics of step A, we must first assess whether PyH$^+$ will actually be available to react via step E instead of reacting via alternative, more favorable reduction pathways. To this end, we computed the reduction potential for reducing PyH$^+$ in solution to adsorbed $o$-DHP ($PyH^+_{\text{sol}} + H^+_{\text{sol}} + 2e^- \rightarrow o$-DHP*) with our mixed implicit-explicit solvation approach for the cluster surface and compared it to the reduction potentials of previously identified PyH$^+$ reduction pathways (Table 7.3). Based on the computed reduction potentials, $PyH^+_{\text{sol}} + H^+_{\text{sol}} + 2e^- \rightarrow o$-DHP* is the most favorable PyH$^+$ reduction pathway. Note that the reduction potentials for the alternative heterogeneous PyH$^+$ reduction pathways were computed with only implicit solvation in Chapter 6 for reasons provided there. Here, we recomputed these reduction potentials with our mixed solvation approach, and we also computed the reduction potential for reducing PyH$^+$ in solution to adsorbed $o$-DHP with only implicit solvation to be able to make truly direct comparisons. We found that the values changed by 0.06 V at most, preserving the same trend mentioned above, namely that $PyH^+_{\text{sol}} + H^+_{\text{sol}} + 2e^- \rightarrow o$-DHP* remains the most favorable pathway for PyH$^+$ reduction. All of the newly reported reduction potentials were computed with the same method presented in section 6.2.2 of Chapter 6.
Table 7.3 Computed reduction potentials ($E^0$) at pH 5.2 for possible PyH$^+$ reduction pathways, including reduction to adsorbed 1,2-(ortho)-dihydropyridine ($o$-DHP), adsorbed pyridine (Py), and 1-pyridinyl radical (1-PyH$^+$). * indicates adsorbed species. Subscript “sol” indicates species in solution. $E^0$s for heterogeneous reduction pathways were computed using our mixed implicit-explicit solvation approach for the cluster surface and $E^0$s obtained with only implicit solvation are reported in parentheses. $PyH^+_{sol} + 1e^- \rightarrow Py^* + H^*$ $E^0$ with only implicit solvation is taken from Chapter 6. $PyH^+_{sol} + 1e^- \rightarrow 1-PyH^*$ $E^0$ (taken from Ref. 17) was computed with an implicit solvation approach and one explicit water molecule.

As discussed in section 1.3.1 of Chapter 1, PyH$^+$ is present in significant concentration in the experimental system, and experimental observations suggest that it is essential for the catalysis. In the proposed mechanism in Figure 7.1, PyH$^+$ is the source of adsorbed Py and adsorbed H, both of which are needed to form the active catalyst adsorbed $o$-DHP. In this chapter, we propose an alternative role for PyH$^+$ that may better explain experimental observations: PyH$^+$ might react with H$^*$ to directly form the proposed active catalyst adsorbed $o$-DHP.
Table 7.4 Reaction ($\Delta G$) and activation ($\Delta G^\dagger$) free energies for relevant surface hydride (H*) transfer reactions, including transfer to adsorbed pyridine (Py) resulting in adsorbed deprotonated 1,2-(ortho)-dihydropyridine (2-PyH-) formation and transfer to PyH+ resulting in adsorbed 1,2-(ortho)-dihydropyridine (o-DHP) formation. $\Delta G$ and $\Delta G^\dagger$ were computed using the “super-molecule (SM) approach” and the “separate reactants (SR) approach”. * indicates adsorbed species. Subscript “sol” indicates species in solution. CO$_2$*perp indicates that CO$_2$ interacts with one Ga surface site in the perpendicular orientation. CO$_2$*parall indicates that CO$_2$ interacts with two Ga surface sites in the parallel orientation. See section 7.3.2.2 for more details on these orientations.

Next, we compare $\Delta G$ and $\Delta G^\dagger$ for forming adsorbed o-DHP either via steps A or E (Table 7.4). To calculate the energetics of step A, we removed one adsorbed H$_2$O from the explicitly solvated cluster surface and replaced it with adsorbed Py. As previously discussed, this choice is justified by the adsorption energies computed in Chapter 4, which show that Py adsorbs
more strongly than H$_2$O. The IS, TS, and FS used to calculate the energetics of step A reported in Table 7.4 are illustrated in Figure 7.9. The product of step E (i.e., o-DHP) requires one surface site for adsorption and adsorbs more strongly than H$_2$O.$^{13,18}$ Thus, we removed one adsorbed H$_2$O from the explicitly solvated cluster and placed PyH$^+$ above it to study this step. Note that PyH$^+$ does not favorably adsorb on this surface and thus should not have access to surface sites; however, PyH$^+$ is bulky enough that it will not be able to approach free adsorption sites because of the steric hindrance from the surrounding adsorbed H$_2$O and OH$^-$. 

Figure 7.9 Side views of the (a) initial state (IS), (b) transition state (TS), and (c) final state (FS) used to calculate the energetics of surface hydride (H$^*$) transfer to adsorbed pyridine (Py) resulting in adsorbed 1,2-(ortho)-dihydropyridine formation (2-PyH$^+$). Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.

The IS, TS, and FS used to calculate the energetics of step E reported in Table 7.4 are illustrated in Figure 7.10. We found that the FS obtained from the TS (by relaxing along one
direction of the eigenvector corresponding to the imaginary frequency) does not have \(o\)-DHP in its most stable adsorption geometry. We thus used a FS with \(o\)-DHP in its most stable adsorption geometry, rather than the one obtained from the TS, to calculate \(\Delta G\).

Figure 7.10 Side views of the (a) initial state (IS), (b) transition state (TS), and (c) final state (FS) used to calculate the energetics of surface hydride (H\(^*\)) transfer to pyridinium (PyH\(^+\)) resulting in adsorbed 1,2-(ortho)-dihydropyridine formation (\(o\)-DHP). Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.

The computed \(\Delta G\)s reveal that step A is nearly thermoneutral (\(\Delta G=+0.7\) kcal/mol, computed with the “SM approach”), while step E is thermodynamically favored (\(\Delta G=-19.9\) kcal/mol, computed with the “SM approach”), which is consistent with the computed \(\Delta G\)_hyd values and the computed PES. The \(\Delta G\) estimates that one can derive from \(\Delta G\)_hyd differences (e.g., difference between H\(^*\) \(\Delta G\)_hyd and adsorbed 2-PyH\(^-\) \(\Delta G\)_hyd to estimate step A \(\Delta G\)) slightly
deviates from the computed $\Delta G$s reported in Table 7.4. This is because $\Delta G_{\text{hyd}}$ differences reveal how much energy is lost or gained by taking a hydride from a species (e.g., H*) and giving it to another species (e.g., adsorbed Py) when these two species are not in contact. In contrast, $\Delta G$s reported in Table 7.4 were computed by simulating the HT between the two explicitly interacting species and should be more reliable. The computed $\Delta G^\dagger$s (+45.3 kcal/mol for step A and +32.1 kcal/mol for step E, computed with the “SM approach”) suggest that adsorbed $\omega$-DHP formation via H* transfer to PyH+ in solution is not only more thermodynamically favored but also more kinetically favored than adsorbed $\omega$-DHP formation via an adsorbed 2-PyH– intermediate (formed by H* transfer to adsorbed Py). Note that the computed PES (Figure 7.7) suggests that step A and step E have similar barriers in the range of 20 kcal/mol, which is different from the trend revealed by the computed $\Delta G^\dagger$s. This difference is attributable to the optimization approach for the structures used to compute the PES. First, these structures were optimized with looser convergence criteria to reduce computational cost; in contrast, the structures used to calculate $\Delta G$s and $\Delta G^\dagger$s were optimized with tighter energy criteria, thus leading to lower energy minima, which were confirmed with a vibrational frequency analysis. Second, all of these structures were optimized with a normal optimization algorithm; in contrast, when computing $\Delta G^\dagger$s, we employed a TS optimization algorithm to identify TS structures, which were confirmed with a vibrational frequency analysis. Furthermore, using properly optimized TS structures also leads to a $\Delta G^\dagger$ trend consistent with the $\Delta G$s, in agreement with Hammond’s postulate: step A, which is nearly thermoneutral, has a higher barrier than step E, which is thermodynamically favored. However, $\Delta G^\dagger$ for step E is still very high and suggests that this process will be kinetically hindered. Using the “SR approach” to calculate step E energetics resulted in a slightly more positive $\Delta G^\dagger$ and less negative $\Delta G$ with no changes to our conclusions. These differences
between the two approaches are due to the fact that the translational and rotational degrees of freedom of PyH⁺ are lost when the TS and FS are formed in the “SR approach”.

In summary, step E (i.e., PyH⁺sol + H* → o-DHP*) is the most favorable pathway for adsorbed o-DHP* formation from H* based on our computed PES and ΔG⁺s; however, adsorbed o-DHP will be unlikely to form via this pathway unless its ΔG⁺ can be lowered under applied potential or overcome by photoexcitation. Independent from whether this ΔG⁺ can be lowered, we must compare it next to ΔG⁺ for transferring H* directly to CO₂ in order to understand whether the formation of adsorbed o-DHP via H* transfer can be a step in the mechanism of CO₂ reduction on p-GaP electrodes.

7.3.2.2 CO₂ Reduction via Surface Hydride Transfer

We placed a CO₂ molecule above the explicitly solvated cluster surface to model CO₂ reduction to HCOO⁻ via H* transfer (CO₂ + H⁻ → HCOO⁻). Furthermore, we added two extra electrons to the explicitly solvated cluster model, which already contains an adsorbed proton, in order to simulate H*, as dictated by microscopic reversibility (vide supra). CO₂ does not favorably adsorb, while the product HCOO⁻ adsorbs more favorably than H₂O via two dative bonds between its oxygen atoms and two Ga surface sites. We thus modeled the CO₂ + H⁻ → HCOO⁻ reaction on the explicitly solvated cluster surface with and without free adsorption sites to get a more accurate estimate of its energetics (IS, TS, and FS for the reaction simulated with and without free adsorption sites are illustrated in Figure 7.11, Figure 7.13, and Figure 7.12).
Figure 7.11 Side views of the (a) initial state (IS), (b) transition state (TS), and (c) final state (FS) used to calculate the energetics of surface hydride (H*) transfer to CO\textsubscript{2} resulting in HCOO\textsuperscript{−} formation on the fully solvated cluster surface. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.

We removed one adsorbed H\textsubscript{2}O as well as the adsorbed OH\textsuperscript{−} hydrogen-bonded to it to free up the two surface sites needed for HCOO\textsuperscript{−} adsorption. Note that while OH\textsuperscript{−} adsorbs more strongly than HCOO\textsuperscript{−}, adsorbed OH\textsuperscript{−} is only stable when forming a hydrogen-bond with a nearby adsorbed H\textsubscript{2}O; if the nearby adsorbed H\textsubscript{2}O is removed (to free the first adsorption site needed for HCOO\textsuperscript{−} adsorption), then adsorbed OH\textsuperscript{−} will get protonated. The newly formed adsorbed H\textsubscript{2}O thus can be removed to free up the second adsorption site needed for HCOO\textsuperscript{−} adsorption. Furthermore, we also removed the proton adsorbed next to adsorbed OH\textsuperscript{−} to remove an overall neutral species. Note that modeling the reaction with and without free adsorption sites also would be required to study the PyH\textsuperscript{+sol} + H\textsuperscript{+} → o-DHP\textsuperscript{*} reaction discussed in the previous
section, given that PyH⁺ does not favorably adsorb while o-DHP adsorbs more strongly than H₂O. However, as previously pointed out, PyH⁺ is bulkier than CO₂ and thus will not be able to approach free adsorption sites because of the steric hindrance from the surrounding adsorbed H₂O and OH⁻.

Figure 7.12 Side views of the (a) initial state (IS), (b) transition state (TS), and (c) final state (FS) used to calculate the energetics of surface hydride (H*) transfer to CO₂ resulting in adsorbed HCOO⁻ formation on the solvated cluster surface with free adsorption sites and CO₂ in the parallel orientation. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.
Figure 7.13 Side views of the (a) initial state (IS), (b) transition state (TS), and (c) final state (FS) used to calculate the energetics of surface hydride (H\(^{\ast}\)) transfer to CO\(_2\) resulting in adsorbed HCOO\(^{-}\) formation on the solvated cluster surface with free adsorption sites and CO\(_2\) in the perpendicular orientation. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.

\(\Delta G\) and \(\Delta G^{\dagger}\) values computed for the CO\(_2\) + H\(^{\ast}\) \(\rightarrow\) HCOO\(^{-}\) reaction (with and without free adsorption sites) are reported in Table 7.4, where they are compared to the energetics for adsorbed 2-PyH\(^{-}\) formation \(\text{via}\) H\(^{\ast}\) transfer to adsorbed Py (Py\(^{\ast}\) + H\(^{\ast}\) \(\rightarrow\) 2-PyH\(^{\ast}\)) and PyH\(^{\dagger}\)\(_{\text{sol}}\) + H\(^{\ast}\) \(\rightarrow\) \(\sigma\)-DHP\(^{*}\). Note that two possible orientations (parallel and perpendicular) for CO\(_2\) interacting with the two free Ga adsorption sites were considered, since we found that they lead to different TSs and FSs. In the parallel orientation, both CO\(_2\) oxygen atoms interact with the surface and CO\(_2\) lies along a Ga row (Figure 7.12). In the perpendicular orientation, only one CO\(_2\) oxygen atom interacts with the surface, and CO\(_2\) lies perpendicular to the Ga rows (Figure
The perpendicular orientation is slightly energetically favored (by 1.6 kcal/mol). The computed $\Delta G$s are consistent with the computed $\Delta G_{\text{hydS}}$: H*- transfer to CO$_2$ is more thermodynamically favored than H* transfer to PyH$^+$. As mentioned earlier, quantitative differences between the $\Delta G$ estimates derived from $\Delta G_{\text{hydS}}$ and the computed $\Delta G$s are attributable to the fact that the latter is computed by simulating the HT between two interacting species while $\Delta G_{\text{hydS}}$ are computed for the isolated species. $\Delta G$ is especially favorable (~40 kcal/mol depending on CO$_2$ orientation, computed with the “SM approach”) with two free Ga adsorption sites due to the large adsorption energy of the product HCOO*$. The $\Delta G^\ddagger$ values are all in the same range (~30 kcal/mol, computed with the “SM approach”) as $\Delta G^\ddagger$ computed for transferring H*- to PyH$^+$ in solution. We found a slightly lower $\Delta G^\ddagger$ (27.0 kcal/mol, computed with the “SM approach”) when CO$_2$ is allowed to interact with two Ga surface sites in the parallel orientation. However, this orientation is less favored, and CO$_2$ would not actually have access to Ga surface sites in an aqueous environment. Also in this case, using the “SR approach” resulted in less negative $\Delta G$s and more positive $\Delta G^\ddagger$s, due to the fact that the translational and rotational degrees of freedom of CO$_2$ are lost when the TS and FS are formed in this approach. However, the overall trend is preserved: except for Py* + H* $\rightarrow$ 2-PyH*, all investigated reactions are thermodynamically favored and have $\Delta G^\ddagger$s all in the same range (~30 kcal/mol).

### 7.3.3 Discussion

Overall, the computed reaction energetics for adsorbed o-DHP formation via H*- transfer and CO$_2$ reduction via H* transfer leads to two important conclusions. First, H*-s are unlikely to play a role in the catalytic mechanism. Second, there is no point in forming adsorbed o-DHP via H* transfer to catalyze the first CO$_2$ reduction step.
The fact that high $\Delta G^\ddagger$s were computed for transferring $H^*$ to $PyH^+$, adsorbed Py, and CO$_2$ suggests that $H^*$ transfer away from the surface is kinetically hindered. This finding is in agreement with previous measurements showing that hydride-like adsorbed protons on GaP(110) are strongly bound to the surface.\textsuperscript{14} The high $\Delta G^\ddagger$ calculated for reducing CO$_2$ \textit{via} $H^*$ transfer is also consistent with the high overpotentials observed for the photoelectrocatalytic reduction of CO$_2$ on p-GaP electrodes in the absence of Py.\textsuperscript{19,20} This finding suggests that, while $H^*$s are unlikely to play a role in the Py-catalyzed CO$_2$ reduction mechanism, they might be the source of protons and electrons in the mechanism at work when Py is not present.

Two results strongly suggest that adsorbed $o$-DHP is unlikely to act as a catalyst for CO$_2$ reduction to HCOO$^-$, if it has to form \textit{via} $H^*$ transfer. First, our computed PESs and $\Delta G^\ddagger$s show that if adsorbed $o$-DHP is formed \textit{via} $H^*$ transfer, then it will most favorably form \textit{via} $H^*$ transfer to $PyH^+$, which does not favorably adsorb on the surface. However, we previously argued that CO$_2$ cannot be directly reduced by $H^*$ transfer because it does not favorably adsorb on the surface and thus will have limited access to $H^*$. Based on this same reasoning, $PyH^+$ should also have limited access to $H^*$, and we must conclude that adsorbed $o$-DHP is unlikely to form \textit{via} $H^*$ transfer to $PyH^+$. Second, $\Delta G^\ddagger$ for adsorbed $o$-DHP formation \textit{via} $H^*$ transfer to $PyH^+$ and $\Delta G^\ddagger$ for CO$_2$ reduction \textit{via} $H^*$ transfer are very similar. Thus, there is no point in forming adsorbed $o$-DHP to catalyze the first step of CO$_2$ reduction given that these two processes will have a similar energy cost; however, if these $\Delta G^\ddagger$s could somehow be reduced and $PyH^+$ could access $H^*$, then adsorbed $o$-DHP might form and catalyze later steps of CO$_2$ reduction with potentially higher barriers. Alternatively, adsorbed $o$-DHP might form \textit{via} a different mechanism with a lower $\Delta G^\ddagger$, or a different intermediate, whose formation does not require $H^*$ transfer, might act as catalyst in this system. As an example, adsorbed 2-$PyH^-$ could
play this role. Our computed $\Delta G_{\text{hyds}}$ suggest that adsorbed 2-PyH$^-$ would be a very strong hydride donor and could be a powerful catalyst for CO$_2$ reduction, assuming that it can be favorably formed via a mechanism other than H$^*$ transfer to adsorbed Py and has a long enough lifetime. We will investigate 2-PyH$^*$ formation and reaction with CO$_2$ on GaP(110) in the next chapter.

7.4 Conclusions

In this chapter, we computed $\Delta G_{\text{hyds}}$ of relevant intermediates and energetics of relevant reaction steps to test a previously proposed mechanism for Py-catalyzed CO$_2$ reduction on p-GaP electrodes. The computed $\Delta G_{\text{hyds}}$ support this mechanism, which relies on H$^*$ transfer to generate the proposed active catalyst adsorbed o-DHP. We found that adsorbed o-DHP formation via concerted $H^+_{\text{sol}}$ and H$^*$ transfers to adsorbed Py is less energetically favored than adsorbed o-DHP formation via H$^*$ to adsorbed Py (followed by spontaneous protonation of adsorbed 2-PyH$^-$) or H$^*$ transfer to PyH$^+$ in solution. However, the overall high $\Delta G^\ddagger$s calculated for transferring H$^*$s to either adsorbed Py (to form adsorbed 2-PyH$^-$), PyH$^-_{\text{sol}}$ (to form adsorbed o-DHP), or CO$_2$ (to form HCOO$^-$) suggest that H$^*$s are unlikely to participate in this chemistry as their transfer away from the surface is severely kinetically hindered. This result also implies that the proposed active catalyst adsorbed o-DHP is either formed via a more kinetically favored mechanism yet to be identified or, if formed at all via H$^*$ transfer, that it plays a role only in later steps of the CO$_2$ reduction mechanism. Alternatively, another Py-derived intermediate whose formation does not require H$^*$ transfer might be the active catalyst in this system; the adsorbed 2-PyH$^-$ species formed from two photoexcited electrons, adsorbed Py, and a solvated proton will be investigated in the next chapter.
7.5 References


Chapter 8

Alternative Co-Catalytic Intermediates***

8.1 Introduction

In Chapter 6, we presented computational results, which, combined with experimental findings by Bocarsly and co-workers,1 provide strong evidence supporting a heterogeneous mechanism that involves adsorbed intermediates for pyridine (Py)-catalyzed CO$_2$ reduction on p-GaP photoelectrodes.2 In Chapter 7, we investigated the potential role of surface hydrides in the catalytic mechanism. We found that a surface hydride transfer to adsorbed Py, which is the reaction step leading to the co-catalyst adsorbed dihydropyridine (DHP) formation in the mechanism proposed by Keith and Carter,3,4 is probably kinetically hindered. More importantly, we found that this step has a similar barrier to the direct transfer of a surface hydride to CO$_2$, which would then indicate no need for the aromatic amine co-catalyst at all, a conclusion at odds with experimental observation. We therefore concluded that either a more kinetically favorable pathway for DHP formation exists or a different Py-derived intermediate that forms via a more kinetically favorable pathway is responsible for catalyzing CO$_2$ reduction.

In this chapter, we investigate two alternative co-catalytic intermediates that might form and react with CO$_2$ in a more energetically favorable way than DHP.3,4 The first intermediate is adsorbed 2-pyridinyl radical (2-PyH’), which was proposed in a recent study by our group.5 Adsorbed 2-PyH’ would play a role similar to that proposed for adsorbed DHP (i.e., shuttling

protons and electrons to CO₂ \textit{via} a hydride transfer). Adsorbed 2-PyH⁺ formation may be easier than adsorbed DHP formation, as it requires fewer proton/electron transfers. Furthermore, a radical species is likely to be more reactive than a closed shell species such as adsorbed DHP. The second co-catalytic intermediate we explore is adsorbed deprotonated DHP (2-PyH⁻), which would also catalyze CO₂ reduction \textit{via} a hydride transfer. 2-PyH⁻, as a closed-shell species, is probably more stable than 2-PyH⁺ and its formation will be more thermodynamically favored. Moreover, adsorbed 2-PyH⁻ is a much better hydride donor than adsorbed DHP, according to our hydricity calculations presented in Chapter 7.

Here, we first introduce the proposed mechanisms of adsorbed 2-PyH⁺-catalyzed and adsorbed 2-PyH⁻-catalyzed CO₂ reduction on p-GaP photoelectrodes. We then use both periodic boundary condition (PBC) calculations and solvated cluster model calculations to characterize the stability and reactivity of these proposed co-catalytic intermediates \textit{via} electron density difference and Bader charge analyses, as well as adsorption free energy calculations. We then calculate the reduction potentials associated with the formation of each intermediate and compare them to the conduction band minimum (CBₘᵢₙ) of GaP(110) computed in Chapter 6 to establish whether these reactions can be catalyzed by photoexcited electrons. We also compare the computed reduction potentials to other previously proposed reactions that might compete with adsorbed 2-PyH⁺ and 2-PyH⁻ formation. Finally, given the more favorable formation thermodynamics of adsorbed 2-PyH⁻, we proceed to compute and compare the reaction energetics for the hydride transfer from adsorbed 2-PyH⁻ to CO₂ and hydride transfer from adsorbed DHP to CO₂.
8.2 Computational Approach

8.2.1 Periodic Boundary Condition Calculations

PBC calculations were employed to study the stability of the 2-PyH⁺ radical in contact with the GaP(110) surface as we did for the 1-pyridinyl radical (1-PyH⁺) in Chapter 6. We simulated electrons and nuclei as described in section 4.2.1 of Chapter 4. We used the same slab model as the one used in Chapter 4 for the study of Py and DHP adsorption and in Chapter 6 for the study of 1-PyH⁺ stability in contact with the GaP(110) surface. Electron density difference and Bader charge analyses were conducted as described in section 6.2.2 of Chapter 6. Note that we used only the less-expensive Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional⁶ for the Bader charge analysis in this study, given that we found that the more expensive PBE0⁷ XC functional gave the same Bader charge analysis results as PBE in Chapter 6. We performed a vibrational frequency analysis and verified the absence of imaginary frequencies to ensure that the adsorbed 2-PyH⁺ structure used in this chapter was a true minimum. As we did in previous chapters for other structures simulated with PBC, we limited the number of atoms included in the vibrational frequency calculation, given the large number of atoms in the unit cell (144). While we included all adsorbate atoms, we only included slab atoms directly interacting with the adsorbate, their nearest neighbors, and their next-nearest neighbors within a 4 Å radius from the adsorbate, yielding a total of 5 Ga atoms and 4 P atoms.

8.2.2 Solvated Cluster Model Calculations

Solvated cluster model calculations were employed to compute electron density difference plots, adsorption free energies, reduction potentials, and reaction energetics. All of the calculations were performed with the same computational details and cluster model as described in section
4.2.2 of Chapter 4. We used our mixed implicit-explicit solvation approach described there (i.e., the Solvation Model based on solute electron Density (SMD)\textsuperscript{8} in the presence of a full monolayer of half-dissociated water molecules) to improve the description of solvation effects when calculating adsorption free energies, reduction potentials, and reaction energetics. We generated the free adsorption sites needed for these calculations by removing water-derived adsorbed species as described in section 4.2.2 of Chapter 4. Adsorption free energies were computed using equation 4.2 from Chapter 4. Electron density difference analyses and standard reduction potentials were computed as reported in section 6.2.1 of Chapter 6. Reaction energetics were computed with the “super-molecule approach” as described in section 7.2 of Chapter 7. Transition state structures were optimized and verified with the same procedure as described there.

8.3 Results and Discussion

8.3.1 Proposed Catalytic Mechanisms

The proposed mechanism for CO\textsubscript{2} reduction to HCOOH via the adsorbed 2-PyH\textsuperscript{−} intermediate is provided in Figure 8.1. In this mechanism, adsorbed 2-PyH\textsuperscript{−} can be formed by either a one-electron reduction and isomerization of pyridinium (PyH\textsuperscript{+}) or by a proton-coupled electron transfer (PCET) to adsorbed Py. Next, adsorbed 2-PyH\textsuperscript{−} transfers a hydride to CO\textsubscript{2}, with an additional electron provided by the negatively biased electrode. Thus, either HCOO\textsuperscript{−} or HCOOH is formed, depending on whether the pH at the electrode/solution interface is low enough to protonate HCOO\textsuperscript{−}.
Figure 8.1 Proposed mechanism of adsorbed 2-pyridinyl radical (2-PyH•) formation and reaction with CO₂. Adsorbed 2-PyH• formation can occur either via a one electron reduction of solvated pyridinium (PyH⁺) or via a proton-coupled electron transfer (PCET) to adsorbed pyridine (Py).

Figure 8.2 Proposed mechanism of adsorbed deprotonated dihydropyridine (2-PyH⁻) formation and reaction with CO₂. Adsorbed 2-PyH⁻ formation can occur either via a two-electron reduction of solvated pyridinium (PyH⁺) or via a proton-coupled two-electron transfer to adsorbed pyridine (Py).

The mechanism for adsorbed 2-PyH⁻ formation and reaction with CO₂ (Figure 8.2) is similar to the mechanism proposed for adsorbed 2-PyH⁺-catalyzed CO₂ reduction (Figure 8.1). In
this mechanism, 2-PyH\textsuperscript{-} is formed either by a two-electron reduction and isomerization of PyH\textsuperscript{+}
or by a proton-coupled, two-electron transfer to adsorbed Py. 2-PyH\textsuperscript{-} transfers a hydride to CO\textsubscript{2} once formed, and either HCOO\textsuperscript{-} or HCOOH is then produced depending on the pH at the interface.

8.3.2 Stability of the Proposed Co-Catalytic Intermediates

The first step towards assessing the feasibility of the proposed mechanisms in Figure 8.1 and Figure 8.2 is to establish whether the proposed catalytic intermediates are stable and favorably adsorb on the GaP(110) surface. In the case of adsorbed 2-PyH\textsuperscript{+}, we must first verify that it is stable as an adsorbed radical on the GaP(110) surface. In Chapter 6, we used electron density difference and Bader charge analyses to study the stability of the previously proposed 1-PyH\textsuperscript{+} radical, finding that it spontaneously transfers its electron to the GaP(110) surface. Here, we used the same tools to investigate the stability of 2-PyH\textsuperscript{+}.

In Figure 8.3, we compare electron density difference plots for 2-PyH\textsuperscript{+} and 1-PyH\textsuperscript{+} adsorbed on the GaP(110) surface, where the surface is modeled with a periodic slab in vacuum. While in the case of 1-PyH\textsuperscript{+} we observe a net electron depletion around the radical and an electron density increase in the proximity of the surface, there is no clear electron transfer in the case of 2-PyH\textsuperscript{+}. This conclusion is supported by the Bader charge analysis: in Chapter 6, we calculated a net transfer of 0.45 e from the radical to the surface for 1-PyH\textsuperscript{+}, while here we calculated a transfer of only 0.02 e for 2-PyH\textsuperscript{+}. Similar results for 2-PyH\textsuperscript{+} were obtained when using our implicitly solvated cluster model of the GaP(110) (Figure 8.4). We therefore conclude that 2-PyH\textsuperscript{+} is indeed stable when in contact with the surface.
Figure 8.3 Electron density difference plots of (a) 2-pyridinyl radical (2-PyH•) and (b) 1-pyridinyl radical (1-PyH•) on top of the GaP (110) periodic slab model in vacuum. Ga atoms are depicted in blue, P atoms in green, C atoms in purple, N atoms in light blue, and H atoms in white. Increase in electron density is depicted in yellow, while decrease in electron density is depicted in blue. Isosurface level = 0.001 e/bohr³. Figure 8.3b is a reproduction of Figure 6.1 from Chapter 6. Figure adapted from Ref. 9. Copyright 2016 American Chemical Society.

Figure 8.4 Electron density difference plot of 2-pyridinyl radical (2-PyH•) adsorbed on the bare GaP(110) surface simulated with (a) a cluster model with continuum solvation and (b) a periodic slab in vacuum. Ga atoms are depicted in blue, P atoms in green, C atoms in purple, N atoms in light blue, and H atoms in white. Increases in electron density are depicted in yellow, decreases in blue. Isosurface level = (a) 0.002 e/bohr³ and (b) 0.001 e/bohr³. Figure 8.4b is a reproduction of Figure 8.3a. Figure adapted from Ref. 9. Copyright 2016 American Chemical Society.
Table 8.1 Adsorption free energies of 2-pyrdinyl radical (2-PyH\(^{\cdot}\)) and deprotonated dihydropyridine (2-PyH\(^{-}\)) on the solvated GaP(110) cluster model at 298.15 K computed using both the implicit and the mixed implicit-explicit solvation schemes.

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption free energy (kcal/mol) at 298.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Implicit solvation</td>
</tr>
<tr>
<td>2-PyH(^{\cdot})</td>
<td>-12.9</td>
</tr>
<tr>
<td>2-PyH(^{-})</td>
<td>-24.3</td>
</tr>
</tbody>
</table>

Having established that 2-PyH\(^{\cdot}\) is stable as a radical adsorbed on the GaP(110) surface, we can now meaningfully compute its adsorption free energy at room temperature to determine whether it can play the role of an adsorbed catalytic intermediate. For the same reason, we also computed the adsorption free energy of 2-PyH\(^{-}\). Both 2-PyH\(^{\cdot}\) and 2-PyH\(^{-}\) adsorb in analogous way to \(\alpha\)-DHP (i.e., via a dative bond from N to a surface Ga, see section 4.7 of Chapter 4). The adsorption free energies (Table 8.1) were computed using both implicit solvation only and our mixed implicit-explicit solvation approach as we did in Chapters 4 and 5 for other adsorbates. We find that both intermediates favorably adsorb on the GaP(110) surface, but 2-PyH\(^{-}\) adsorbs significantly more strongly. This finding is justified by the fact that 2-PyH\(^{-}\), being a negatively charged species, has a larger driving force to form a strong dative bond with a surface Ga atom, which carries a partial positive charge. We observed that the two solvation approaches give the same trend, in agreement with the results found in Chapters 4 and 5. In the case of 2-PyH\(^{-}\), including the explicit layer of adsorbed water molecules has a greater stabilization effect due to the hydrogen bond formed between one of the two 2-PyH\(^{-}\) N lone pairs and a co-adsorbed water.
molecule. Overall, based on the computed adsorption free energies, we conclude that both 2-PyH⁺ and 2-PyH⁻ are plausible candidates as the active adsorbed co-catalyst in this system.

8.3.3 Formation Thermodynamics of the Proposed Co-Catalytic Intermediates

Next, we determine whether formation of adsorbed 2-PyH⁺ and 2-PyH⁻ on GaP(110) are thermodynamically feasible under experimental conditions by computing reduction potentials associated with their hypothesized formation paths from solvated PyH⁺ and adsorbed Py (Figure 8.1 and Figure 8.2, respectively). We also compare these reduction potentials to the reduction potentials associated with reducing adsorbed Py to adsorbed 1,2-(ortho)-dihydropyridine (o-DHP) and various PyH⁺ reduction pathways previously proposed in this dissertation and other studies (Table 8.2). Note that, as we have done in previous chapters, here we will only consider one of the two possible isomers of DHP: o-DHP. A justification for this choice is provided in section 4.7 of Chapter 4.

We can determine whether adsorbed 2-PyH⁺ and 2-PyH⁻ formation are feasible under experimental conditions by comparing the computed reduction potentials associated with their formation (Table 8.2) to the CB_{min} of solvated GaP(110) computed in Chapter 6 (-1.66 V vs. SCE at pH = 5.2). We find that the GaP(110) CB_{min} resides at a negligibly more negative reduction potential than the reduction potential associated with adsorbed 2-PyH⁺ formation via PCET to adsorbed Py (-1.62 V vs. SCE), probably excluding this pathway. The CB_{min} of GaP(110) resides at a relatively more negative reduction potential than that associated with adsorbed 2-PyH⁺ formation via a one-electron transfer to PyH⁺ (-1.29 V vs. SCE). We thus conclude that formation of adsorbed 2-PyH⁺ is thermodynamically feasible via the one-electron transfer to solvated PyH⁺ but, similar to 1-PyH⁺ formation, the process is not strongly exoergic.
In the case of adsorbed 2-PyH⁻, we predict that either formation pathway has a reduction potential less negative than GaP(110) CBₘᵟᵳ (−1.09 V and −0.86 V vs. SCE for formation via adsorbed Py reduction and PyH⁺ reduction, respectively). We therefore expect both pathways to be thermodynamically viable. However, formation via PyH⁺ reduction is again more thermodynamically favored and thus likely represents the preferred pathway for 2-PyH⁻ formation. Furthermore, the reduction potentials for adsorbed 2-PyH⁻ formation are less negative than the reduction potentials for 2-PyH⁺ formation (0.53 V and 0.43 V difference for formation via adsorbed Py reduction and PyH⁺ reduction, respectively) as expected, given the closed-shell nature of 2-PyH⁻ and the radical nature of 2-PyH⁺.

A comparison of the reduction potentials reported in Table 8.2 suggests that formation of adsorbed o-DHP is the most thermodynamically favorable step and that adsorbed o-DHP is more likely to be the dominant catalytic species in this system. However, while the reduction potentials for adsorbed 2-PyH⁺ formation are significantly more negative than the reduction potentials for adsorbed o-DHP formation (0.65 V and 0.56 V difference for formation via adsorbed Py reduction and PyH⁺ reduction, respectively), there is a much smaller difference between the reduction potentials for adsorbed 2-PyH⁻ formation and adsorbed o-DHP formation (0.12 V and 0.13 V difference for formation via adsorbed Py reduction and PyH⁺ reduction, respectively). These results suggest that adsorbed 2-PyH⁻ formation might be able to compete with adsorbed o-DHP formation. Furthermore, 2-PyH⁻ formation might be more kinetically favored as it requires the transfer of less protons and electrons. This aspect is the subject of an ongoing investigation in our group. On the other hand, as already discussed in Chapter 7, the relatively large pKᵦ calculated in Chapter 5 for adsorbed o-DHP (13.4) suggests that 2-PyH⁻ might get protonated once formed, ultimately resulting in adsorbed o-DHP formation.
Ultimately, assessing the kinetics of protonation and the attendant lifetime of 2-PyH\(^+\) will be key to determining whether this species is involved in the catalysis.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E^0) (V vs. SCE) at pH=5.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Py}^* + 2\text{H}^+_{\text{sol}} + 2e^- \rightarrow \text{o-DHP}^*)</td>
<td>-0.97 (-1.01)</td>
</tr>
<tr>
<td>(\text{Py}^* + \text{H}^+_{\text{sol}} + e^- \rightarrow \text{2-PyH}^*)</td>
<td>-1.62 (-1.74)</td>
</tr>
<tr>
<td>(\text{Py}^* + \text{H}^+_{\text{sol}} + 2e^- \rightarrow \text{2-PyH}^*)</td>
<td>-1.09 (-1.41)</td>
</tr>
<tr>
<td>(\text{PyH}^+_{\text{sol}} + 1e^- \rightarrow \text{Py}^* + \text{H}^*)</td>
<td>-0.91 (-0.85)</td>
</tr>
<tr>
<td>(\text{PyH}^+<em>{\text{sol}} + \text{H}^+</em>{\text{sol}} + 2e^- \rightarrow \text{o-DHP}^*)</td>
<td>-0.73 (-0.79)</td>
</tr>
<tr>
<td>(\text{PyH}^+_{\text{sol}} + 1e^- \rightarrow \text{2-PyH}^*)</td>
<td>-1.29 (-1.31)</td>
</tr>
<tr>
<td>(\text{PyH}^+_{\text{sol}} + 2e^- \rightarrow \text{2-PyH}^*)</td>
<td>-0.86 (-1.04)</td>
</tr>
<tr>
<td>(\text{PyH}^+<em>{\text{sol}} + 1e^- \rightarrow \text{1-PyH}^*</em>{\text{sol}})</td>
<td>-1.44</td>
</tr>
</tbody>
</table>

Table 8.2 Computed reduction potentials (\(E^0\)) relative to the saturated calomel electrode (SCE) at pH 5.2 for possible adsorbed pyridine (Py) and pyridinium (PyH\(^+\)) reduction pathways, including reduction to adsorbed 1,2-(ortho)-dihydropyridine (o-DHP), adsorbed 2-pyridinyl radical (2-PyH\(^-\)), adsorbed deprotonated dihydropyridine (2-PyH\(^-\)), and the solvated 1-pyridinyl radical (1-PyH\(^-\)). * indicates adsorbed species. Subscript “sol” indicates species in solution. \(E^0\)s for heterogeneous reduction pathways were computed using our mixed implicit-explicit solvation approach for the cluster surface and \(E^0\)s obtained with only implicit solvation are reported in parentheses. \(\text{PyH}^+_{\text{sol}} + 1e^- \rightarrow \text{Py}^* + \text{H}^*\) \(E^0\) is reproduced from Chapter 6, and \(\text{PyH}^+_{\text{sol}} + \text{H}^+_{\text{sol}} + 2e^- \rightarrow \text{o-DHP}^*\) \(E^0\) is reproduced from Chapter 7. \(\text{PyH}^+_{\text{sol}} + 1e^- \rightarrow \text{1-PyH}^*\) \(E^0\) (taken from Ref. 10) was computed with an implicit solvation approach and one explicit water molecule.
8.3.4 Reaction of Adsorbed Deprotonated Dihydropyridine and Adsorbed Dihydropyridine with CO₂

The computed reduction potentials reported in Table 8.2 suggest that adsorbed 2-PyH⁻ formation is more thermodynamically favored than adsorbed 2-PyH⁺ formation, and therefore adsorbed 2-PyH⁻ is more likely to play the role of adsorbed catalytic species in this system. Based on these results, we now focus on calculating the energetics of CO₂ reduction to HCOO⁻ via hydride transfer from adsorbed 2-PyH⁻ to establish whether the latter can effectively catalyze this reaction. Furthermore, given that adsorbed o-DHP formation is expected to compete with adsorbed 2-PyH⁻ formation, here we also compute the energetics for CO₂ reduction to HCOO⁻ via hydride transfer from adsorbed o-DHP and compare these results. The Table 8.1 reaction free energies (ΔGs) and activation free energies (ΔG‡s) at room temperature computed using our mixed implicit-explicit solvation approach for these two reactions are reported in Table 8.3. The structures used to calculate the energetics for hydride transfer from adsorbed 2-PyH⁻ to CO₂ and from adsorbed o-DHP to CO₂ are reported in Figure 8.5 and Figure 8.6, respectively.

We find that CO₂ reduction to HCOO⁻ via hydride transfer from adsorbed 2-PyH⁻ is both thermodynamically and kinetically more favored than CO₂ reduction to HCOO⁻ via hydride transfer from adsorbed o-DHP. These findings are not surprising given that 2-PyH⁻ is a negatively charged species equivalent to deprotonated o-DHP and thus will have a much larger driving force to transfer a hydride to CO₂. Our computed ΔGs and ΔG‡s therefore confirm what we already predicted in Chapter 7 based on our calculated thermodynamic hydricities: adsorbed 2-PyH⁻ is a much better catalyst for CO₂ reduction via hydride transfer than adsorbed o-DHP.
Table 8.3 Computed reaction free energies (ΔG) and activation free energies (ΔG‡) at room temperature (298.15 K) for reaction of adsorbed deprotonated dihydropyridine (2-PyH⁻) and adsorbed 1,2-(ortho)-dihydropyridine (o-DHP) with CO₂ to form HCOO⁻. * indicates adsorbed species. Subscript “sol” indicates species in solution. ΔG and ΔG‡ were computed using the GaP(110) cluster model solvated with our mixed implicit-explicit approach, as described in section 4.2.2.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG (kcal/mol)</th>
<th>ΔG‡ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-PyH⁻* + CO₂,sol → Py* + HCOO⁻,sol</td>
<td>-26.9</td>
<td>+7.6</td>
</tr>
<tr>
<td>o-DHP* + CO₂,sol → PyH⁺,sol + HCOO⁻,sol</td>
<td>-10.2</td>
<td>+25.2</td>
</tr>
</tbody>
</table>

Figure 8.5 Top view of the (a) initial state, (b) transition state, and (c) final state used to calculate the energetics for the reaction of adsorbed deprotonated dihydropyridine (2-PyH⁻) with CO₂ to form adsorbed pyridine (Py) and HCOO⁻ on the GaP(110) cluster model solvated with our mixed implicit-explicit approach. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.
Figure 8.6 Top view of the (a) initial state, (b) transition state, and (c) final state used to calculate the energetics for the reaction of adsorbed 1,2-(ortho)-dihydopyridine (o-DHP) with CO$_2$ to form pyridinium (PyH$^+$) and HCOO$^-$ on the GaP(110) cluster model solvated with our mixed implicit-explicit approach. Ga atoms are represented in blue, P atoms in green, C atoms in purple, N atoms in light blue, O atoms in red, and H atoms in off-white.

### 8.4 Conclusions

In this chapter, we proposed and investigated the viability of two newly proposed heterogeneous mechanisms for CO$_2$ reduction on p-GaP photoelectrodes based on adsorbed 2-PyH$^+$ and adsorbed 2-PyH$^-$ catalytic intermediates. We found that, in contrast to 1-PyH$^+$, 2-PyH$^+$ is a stable radical species on the GaP(110) surface based on electron density difference and Bader charge analyses. Both 2-PyH$^+$ and 2-PyH$^-$ were found to favorably adsorb on GaP(110) at room temperature, with 2-PyH$^-$ having a larger adsorption free energy. We therefore concluded that they are both plausible candidates as adsorbed catalysts in this system. The computed reduction potentials show that both adsorbed 2-PyH$^+$ and adsorbed 2-PyH$^-$ can form on the GaP(110) surface by transfer of photoexcited electrons but adsorbed 2-PyH$^-$ formation is significantly more favored and might compete with adsorbed o-DHP formation. However, adsorbed o-DHP
formation remains the most thermodynamically favored step and might occur via protonation of adsorbed 2-PyH\(^-\) based on the previously computed \(\sigma\)-DHP \(pK_a\). On the other hand, we cannot exclude that adsorbed 2-PyH\(^-\) formation might be more kinetically favored because it requires less protons and electrons. As such, this aspect is currently under investigation in our group. Based on these results, we computed and compared the reaction energetics for CO\(_2\) reduction to HCOO\(^-\) via hydride transfer from adsorbed 2-PyH\(^-\) and adsorbed \(\sigma\)-DHP. We found that CO\(_2\) reduction via hydride transfer from adsorbed 2-PyH\(^-\) is more favored both from the kinetics and thermodynamics points of view. This finding confirms our prediction based on the computed thermodynamic hydricities that 2-PyH\(^-\), if formed and with a long-enough lifetime before being protonated, would be a better catalyst than adsorbed \(\sigma\)-DHP for CO\(_2\) reduction via hydride transfer.

8.5 References


Chapter 9

Conclusions

In this dissertation, we used quantum-mechanics-based methods to investigate a promising photoelectrocatalytic system for the selective reduction of CO₂ to methanol. Our main goal was to provide useful mechanistic insights on this system to inform the design of improved photoelectrocatalysts for CO₂ reduction, thus ultimately contributing to the development of a technology for the sustainable production of liquid fuels.

The specific system under investigation was developed by Professor Andrew B. Bocarsly’s research group at Princeton University. In this system, CO₂ is selectively reduced to methanol by using a p-GaP photocathode under illumination and in contact with an acidified aqueous solution containing pyridine (Py). This system is an excellent photoelectrocatalyst for CO₂ reduction: it has a high selectivity (nearly 100% Faradaic efficiency towards CO₂ reduction to methanol) and it works at underpotentials (i.e., requires an applied potential less negative than the thermodynamic reduction potential for methanol). Selective CO₂ reduction on p-GaP photocathodes was previously observed also in the absence of Py, although high overpotentials had to be applied. Therefore, it was concluded that Py, or a species derived from it, must have a crucial role in the catalytic mechanism. The promising features of the photoelectrocatalytic system developed by Bocarsly and co-workers as well as the puzzling role of Py have motivated numerous studies in the past decades, with several mechanisms proposed to explain the observations. This dissertation represents a significant step forward towards elucidating the Py-catalyzed CO₂ reduction mechanism by shedding light on relevant mechanistic aspects that were
still under debate at the time when this work began, providing key evidence that rules out previously proposed mechanisms, as well as hypothesizing and testing new ones.

This thesis work began with two studies necessary for developing a proper model of the electrode surface to be used in the subsequent investigations. Throughout this dissertation, we selected the GaP(110) surface to model the electrode surface, because experimental evidence demonstrates that it represents both the most stable\(^4\) – and therefore the most likely exposed facet for polycrystalline electrodes - and the most active surface of GaP.\(^5\) These first two studies also provided useful mechanistic insights.

In the first study (Chapter 3), we characterized the GaP (110)/H\(_2\)O interface in collaboration with the experimental research group of Professor Bruce E. Koel at Princeton University. Determining the water structure that forms on the GaP(110) surface was necessary to properly model the surface of the p-GaP photocathode exposed to the aqueous solution. Furthermore, water-derived species adsorbed on the electrode surface can affect photoexcited electron transfer energetics and can also be directly involved in the reaction mechanism, especially if the latter is heterogeneous, as suggested by experimental observations. We used density functional theory (DFT) with periodic boundary condition (PBC) calculations to compute a surface-adsorbate phase diagram illustrating the most stable water configuration on the surface under different conditions, ranging from water-poor to water-rich conditions.

The computed phase diagram showed that water adsorption and dissociation is always (\textit{i.e.,} both under water-poor and water-rich conditions) thermodynamically favored on the GaP(110) surface as long as the Ga-OH species formed upon water dissociation are stabilized by a hydrogen bond with a co-adsorbed undissociated water molecule. In particular, the most
thermodynamically stable water configuration identified by the phase diagram under all conditions is a full monolayer of half-dissociated water molecules, resulting in a mixture of Ga-OH, Ga-H₂O, and P-H species formed at the GaP(110)/H₂O interface. All of these species were observed in the ambient pressure photoelectron spectroscopy experiments conducted by our collaborators under ultrahigh vacuum and at low pressure (i.e., under simulated water-poor conditions), thus validating predictions based on the computed phase diagram. We therefore concluded that this half-dissociated water configuration will form on the surface of the p-GaP photocathode when exposed to an aqueous solution (i.e., under water-rich conditions) in the system developed by Bocarsly and co-workers. Based on these results, we included an adsorbed monolayer of half-dissociated water molecules in our model of the electrode surface employed in the subsequent investigations. Furthermore, the formation of P-H species at the GaP(110)/H₂O interface predicted by our computed phase diagram and confirmed by experimental observations offered partial validation of the mechanism proposed by Keith and Carter.⁶,⁷ In their proposed mechanism, surface hydrides formed upon water dissociation are directly involved in the formation of the postulated active catalyst, adsorbed dihydropyridine (DHP).

In the second study (Chapter 4), we characterized the adsorption geometries and binding energies of various species relevant to the catalytic mechanism based on the experimental conditions¹ and the proposed mechanism on GaP electrodes.⁶,⁷ For this purpose, we used a periodic slab model of the GaP(110) surface in vacuum with pure DFT and a solvated cluster model of this surface with hybrid DFT. The cluster model was developed based on a procedure previously established by the Carter group.⁸ We showed that the same adsorption free energy trend is obtained when using either model of the surface and specific adsorption free energy differences were explained based on different exchange-correlation functional and solvation
choices. We therefore concluded that our solvated cluster model could be trusted to simulate the GaP(110) periodic surface, and we employed the model throughout this thesis work for accurate calculations of thermodynamic properties of surface-adsorbed species and reaction energetics.

We then showed that the same adsorption free energy trend holds when using the cluster model to simulate relevant experimental conditions (i.e., a negatively charged catalytic photocathode in contact with water that is half-dissociatively adsorbed on its surface). We therefore concluded that the computed adsorption free energy trend was robust and could be used to draw mechanistic insights on the experimental system. Both CO$_2$ and pyridinium (PyH$^+$) were found to prefer to stay in solution rather than adsorb on the GaP(110) surface whereas H$_2$O, Py, and DHP were predicted to absorb relatively strongly via dative bonding. These results suggested the potential need for an adsorbed co-catalyst to shuttle electrons from the surface to CO$_2$, given that various adsorbed species (e.g., OH$^-$, H$_2$O, Py, and DHP) might prevent CO$_2$ from accessing the surface. Bocarsly and co-workers previously proposed that PyH$^+$ (pK$_a$= 5.3) in solution might play an essential catalytic role because reduction phenomena were only observed when the pH of the aqueous solution containing Py was below 7. The adsorption free energy trend, however, suggests that PyH$^+$ at least will not be an adsorbed co-catalyst. In contrast, both Py and DHP could be valid Py-based adsorbed co-catalysts for CO$_2$ reduction in this system.

The interaction between Py and the GaP(110) as well as the reactivity of adsorbed Py were characterized further in a combined computational-experimental study (Chapter 4). Professor Bruce E. Koel’s group at Princeton University performed scanning tunneling microscopy measurements of the GaP(110) surface exposed to Py; we then used computed partial electron densities of states in relevant energy ranges to interpret their experimental
observations. These results revealed that adsorbed Py is reactive towards nucleophilic attack by a surface hydride or another hydride equivalent, thus supporting the mechanism for adsorbed DHP formation via surface hydride transfer to adsorbed Py as hypothesized by Keith and Carter.\textsuperscript{6,7}

Our study of the GaP(110)/H\textsubscript{2}O interface (Chapter 3) showed that protons adsorb onto phosphorus atoms when the GaP(110) surface is exposed to water, but did not offer any additional insights into the stability of these species when other relevant experimental conditions (\textit{i.e.}, surface negative charge and presence of co-adsorbed species) are taken into account. This was an important point to address in order to further validate the mechanism proposed by Keith and Carter, which relies on these adsorbed species for the formation of the active catalyst.\textsuperscript{6,7} We established the stability of the adsorbed protons formed upon heterolytic water dissociation on the GaP(110) surface by comparing their computed acidity constant to the acidity constants of other relevant species (Chapter 5). We showed that, under typical experimental conditions, their acidity constant is significantly larger than the acidity constant of other protic species present in the system. We therefore concluded that these adsorbed protons are very stable under experimental conditions and could potentially be reduced to the surface hydrides needed for adsorbed DHP formation in the mechanism proposed by Keith and Carter.\textsuperscript{6,7} The high stability of the adsorbed proton also suggests that the protons needed in the mechanism of CO\textsubscript{2} reduction are unlikely to come from the surface, and thus another proton source (\textit{e.g.}, solution) is required.

Specific mechanistic steps involving PyH\textsuperscript{+} have been proposed,\textsuperscript{9–12} based on experimental evidence suggesting that an acidic pH is needed for catalytic CO\textsubscript{2} reduction to occur.\textsuperscript{9} In this dissertation, we used a variety of computational tools with both PBC and solvated cluster model calculations to explore the possible mechanistic role of PyH\textsuperscript{+} (Chapter 6). We first
demonstrated that reduction of PyH⁺ to the 1-pyridinyl radical (1-PyH⁺), a mechanistic step proposed in previous studies,⁹⁻¹¹ is unlikely to occur. In particular, accurate PBC calculations with both pure and hybrid DFT as well as solvated cluster model calculations showed that 1-PyH⁺ is unstable and spontaneously transfers its electron to the GaP(110) surface, in agreement with a previous study by our group.⁸ Furthermore, we discovered that the previously computed reduction potential for PyH⁺ reduction to 1-PyH⁺¹³ is only slightly less negative than the conduction band minimum (CB min) of solvated GaP(110), which was computed in this work using accurate non-self-consistent GW (G₀W₀) theory. This result indicates that there is only a small, perhaps even nonexistent, thermodynamic driving force for this homogeneous reduction reaction to occur, as the driving force (~0.2 eV) is within the margin of error of the reduction potential calculations.¹³ Furthermore, our earlier investigation (Chapter 4) determined that PyH⁺ adsorption is unfavorable even when the photocathode is negatively charged, thus suggesting that reduction of PyH⁺ is not aided by adsorption. We therefore investigated alternative PyH⁺ reduction pathways based on the mechanism proposed by Batista and co-workers on Pt.¹² We discovered that reduction of PyH⁺ to an adsorbed H atom and adsorbed Py is the most thermodynamically favored one-electron reduction pathway for PyH⁺ and is much more likely to occur, based on its computed reduction potential relative to the GaP(110) CBₘᵦᵣ. We also pointed out that this pathway produces the intermediates needed for DHP formation in the mechanism proposed by Keith and Carter,⁶,⁷ which we continued to investigate in the remainder of this thesis work.

Another aspect of the mechanism that has been the subject of debate is whether the electrode surface has a catalytic role. The electrode dependence of selectivity and applied potential demonstrated by different experimental reports suggests that the electrode surface is
In this thesis work, we provided strong evidence supporting the hypothesis of a heterogeneous mechanism by comparing various computed properties of the GaP(110) and GaP(111) surfaces (Chapter 6). In particular, we discovered that these two surfaces have nearly the same CB_{\text{min}}. This result suggests that the two surfaces should display the same activity towards CO_{2} reduction if the catalytic mechanism was fully homogeneous and if the only role of the electrode was to provide photoexcited electrons for the reduction to occur. However, Bocarsly and co-workers observed different activity towards CO_{2} reduction for the two surfaces.\textsuperscript{5} We therefore concluded that the catalytic mechanism cannot be fully homogeneous, and adsorbed intermediates must play a mechanistic role. Our results suggest that the observed difference in activity could be explained by different adsorption free energies of relevant intermediates calculated for the two surfaces.

Having concluded that the mechanism must involve adsorbed intermediates and that a viable pathway for PyH^{+} reduction leads to the reactants needed for adsorbed DHP formation, we continued investigating the mechanism proposed by Keith and Carter.\textsuperscript{6,7} We used computed thermodynamic hydricities of relevant species to show that adsorbed DHP formation via surface hydride transfer and hydride transfer from DHP to CO_{2} are both thermodynamically favorable steps, thereby concluding that the mechanism proposed by Keith and Carter is thermodynamically feasible (Chapter 7). We then proceeded to evaluate the full energetics for adsorbed DHP formation via surface hydride transfer. We discovered that the most energetically favorable pathway for DHP formation via surface hydride transfer is a surface hydride transfer to PyH^{+}. This also represents the most favorable pathway for PyH^{+} reduction identified so far, according to our computed reduction potentials. However, the high-activation free energy for this pathway (~30 kcal/mol) suggests that this process is unlikely to occur unless the former can be
reduced under experimental conditions. More importantly, this step was found to have a similar barrier to the direct surface hydride transfer to CO₂, which would imply that adsorbed DHP is unnecessary, at least for the first CO₂ reduction step. These results suggested that another intermediate that forms via a more favorable pathway is likely to be the active catalyst in this system. Our computed thermodynamic hydricities suggests that adsorbed deprotonated DHP (2-PyH⁻) is a promising candidate as an alternative catalytic intermediate for CO₂ reduction. Alternatively, adsorbed DHP might be formed via a more favorable pathway that does not require surface hydride transfer, which appears to be hindered kinetically unless the computed activation free energies can be lowered under experimental conditions.

Having discovered that adsorbed DHP formation via surface hydride transfer might be hindered kinetically, we then moved on to investigate two newly proposed alternative catalytic intermediates: an adsorbed 2-pyridinyl radical (2-PyH⁺) and adsorbed 2-PyH⁻ (Chapter 8). The formation of these intermediates might be more kinetically favored because their proposed formation mechanisms require less protons and electrons than adsorbed DHP. We first showed that 2-PyH⁺ is stable as an adsorbed radical on the GaP(110) surface and that both intermediates favorably adsorb on this surface at room temperature. Thus, we proceeded to determine the thermodynamic driving force for forming these intermediates by comparing the reduction potentials associated with their proposed formation pathways to the GaP(110) CBₘᵋᵣ. Our results suggest that both intermediates could form under experimental conditions with 2-PyH⁻ formation being more thermodynamically favorable, an expected result given the closed-shell nature of 2-PyH⁻. Adsorbed o-DHP formation, however, remains the most thermodynamically favored step. Furthermore, the relatively high pKₐ computed for adsorbed DHP (Chapter 5) suggests that adsorbed 2-PyH⁻ might undergo protonation, producing adsorbed DHP. Based on these results,
we proceeded to compare the computed reaction energetics for hydride transfer to CO\(_2\) from adsorbed 2-PyH\(^-\) and adsorbed o-DHP. These results confirmed our prediction based on the thermodynamic hydricities computed in our earlier investigation (Chapter 7): hydride transfer from adsorbed 2-PyH\(^-\) to CO\(_2\) has a lower activation energy and is more thermodynamically favorable. We therefore concluded that if 2-PyH\(^-\) formation is kinetically viable, and this species has a long-enough lifetime before being protonated, then this intermediate is a plausible co-catalyst in the mechanism of Py-catalyzed CO\(_2\) reduction.

In summary, many novel insights into the mechanism of Py-catalyzed CO\(_2\) reduction on p-GaP photoelectrodes were presented in this dissertation. We provided strong evidence disfavoring the long-standing hypothesis of PyH\(^+\) reduction to 1-PyH\(^-\), which was already ruled out for metal electrodes but was still considered for semiconductor electrodes. We also demonstrated that the mechanism must be heterogeneous and we presented numerous results that supported the mechanism proposed by Keith and Carter,\(^6,7\) which was the only heterogeneous mechanism for Py-catalyzed CO\(_2\) reduction on p-GaP photoelectrodes proposed to date when this thesis work began. However, we also found that the formation of the active catalyst in this proposed mechanism is likely kinetically hindered. We therefore proposed and investigated alternative catalytic intermediates that could form more easily and be more reactive towards CO\(_2\) reduction. Adsorbed 2-PyH\(^-\) appears especially promising, but two queries remain open and must be addressed in future studies: 1) whether the formation of this intermediate is kinetically favorable; and 2) whether this intermediate has a long-enough lifetime to react with CO\(_2\) before being protonated, resulting in adsorbed DHP. The investigation of the mechanistic steps beyond HCOOH formation and ultimately leading to methanol formation will also be necessary to establish the validity of this newly proposed catalytic intermediate. Finally, an important point
that should be addressed in future investigations is the energetics of the hydrogen evolution reaction (HER) on the GaP(110) surface. The high selectivity observed in the experiments by Bocarsly and co-workers suggests that this reaction is more kinetically hindered than CO₂ reduction. The generally high-activation free energies for surface hydride transfer reactions obtained in this work could explain this observation, assuming that HER occurs via the Volmer-Heyrovsky mechanism (i.e., direct reaction of a proton in solution with the P-H group on p-GaP photocathodes). However, an actual comparison of activation free energies will be needed to confirm this hypothesis.

Overall, this dissertation contributes in many ways to the overarching goal of developing technologies for sustainable liquid fuel production via photoelectrocatalytic CO₂ reduction. First, it provided significant insights into the mechanism of CO₂ reduction in the promising system developed by Bocarsly and co-workers, as summarized in the previous paragraph. Second, this dissertation established an array of models and computational tools that may be used to investigate other promising photoelectrocatalytic systems for CO₂ reduction. This aspect is demonstrated by a recent mechanistic study of Py-catalyzed CO₂ reduction on the GaP(111) and CdTe(111) surfaces reported by our group. In this study, reduction potentials of relevant reactions at these surfaces were computed using a solvated cluster model built with the same procedure as the one employed in this dissertation; these reduction potentials were then compared to the respective computed surface CBmin to determine which reduction reactions are thermodynamically feasible, thus following the same strategy used in this dissertation. Finally, we hope that the combined experimental-theoretical studies conducted in this dissertation will serve as inspiration and guidance for future collaborative projects on this and other promising systems for the photoelectrocatalytic reduction of CO₂ to liquid fuels.
9.1 References


