Catalysis by $\text{Au}_2^-$
An ab initio atomistic thermodynamics study
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Introduction

Catalysis is of fundamental importance to many chemical processes. In almost 90 % of all chemical processes in industry, a catalyst is involved. However, many of these catalytic reactions are still poorly understood. Due to recent advances in computer power and computational methods used, computer simulations have become an invaluable tool to gain insight in catalytic reactions.

This work is a computational study towards the atomistic understanding of a catalytic process. The reaction studied is the oxidation of carbon monoxide, catalyzed by gold dimer anions (Au$_2^-$). A systematic approach fully from first principles is used to predict the structure of the catalyst and possible reaction intermediates.

Chapter 1 gives background information about catalysis, the CO oxidation reaction and gold.

Chapter 2 introduces the computational methods that are used in this study. Density functional theory, the code used and how to model the environment with ab initio atomistic thermodynamics are explained.

Chapter 3 shows the results of this method. It contains the phase diagrams which are obtained for Au$_2^-$, gives the structure of the catalyst and possible reaction intermediates. Possible reaction mechanisms are suggested as a starting point for kinetic studies. The limits of the method and comparison with previous works are also treated here.

Chapter 4 concerns water, which is always present in realistic environments. Its effect on the enhancement of the CO oxidation reaction is poorly understood.

Chapter 5 contains a summary and conclusions.
1.1 Gold Clusters and Catalysis

1.1.1 What is catalysis?

Catalysis is the enhancement of the rate of a chemical reaction by the addition of a catalyst. Adding a catalyst lowers the activation energy without changing the catalyst, which can be used over and over again. The lower barrier results in an increased reaction rate and a reduction of the activation energy necessary, hereby increasing the efficiency of a process. Catalysts can also be used to make the reaction path leading to one enantiomer much more favourable than the path to the other mirror image, thus offering improved selectivity. Further, it can be used to block side reactions. The lower activation barrier can be achieved in many different ways: by holding the reactants in close proximity, by holding them in the right configuration to react, by making bonds easier to break, by transferring electrons and by acting as an efficient means for energy transfer, for example \[1\].

A common way for a catalyst to work is that the reactants adsorb on the surface of the catalyst, where they react to form the product. In order for this to function, reactants should not be bound too loosely to the catalyst, otherwise they will not adsorb on the catalyst. They also should not bind too tight, because this would prevent the release of the product. This is known as the Sabatier principle.

A distinction is made between homogeneous catalysis, where the reactants and the catalyst are in the same phase, and heterogeneous catalysis, where this is not the case. For the latter, it is common that the reactants are gases whereas the catalyst is a solid. Heterogeneous catalysis is much more common in industry than homogeneous catalysis, because it is easier to separate product and catalyst after the reaction. This means the catalyst can be recycled more easily, which greatly reduces the cost and increases efficiency.

Lower energy barriers and improved selectivity mean that less energy is required, less waste is produced and more product is obtained. This makes a process more efficient and environmentally friendly and consequently, the use of catalysts is widespread. Despite of this, the role of the catalyst is often poorly understood.

1.1.2 CO oxidation

Even a relatively simple reaction, such as the conversion of carbon monoxide to carbon dioxide, can still present a challenge to scientists. Although the gain in energy in this reaction,

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\]

is high (−3.27 eV), it will not occur in normal conditions. This is due to the different spin states of the reactants: The ground state of CO is a singlet and that of O\(_2\) is a triplet. Conservation of spin requires that the reaction product is a triplet, but CO\(_2\) is a singlet. This makes the reaction spin-forbidden. This can be circumvented by splitting O\(_2\) into one O radical singlet and one O radical triplet. However, two oxygen radicals are much higher in energy than O\(_2\). This means that a large barrier needs to be overcome in the CO oxidation reaction.

It is often desirable for this CO oxidation to occur, because CO is toxic. This causes problems in fuel cells for instance, where the membrane is poisoned by CO. The process can also be used in indoor air quality applications.
1.1. GOLD CLUSTERS AND CATALYSIS

1.1.3 Gold

It came as a surprise when Haruta et al. discovered in 1987 that gold clusters are also capable of catalyzing CO oxidation\(^2\). The inertness and nobility of bulk gold make it very suitable for coins and jewelry, but these very features also made it seem very improbable that gold would participate in chemical reactions.

Gold is the 79\(^{th}\) element in the periodic table and has an electron configuration of \([\text{Xe}]4f^{14}5d^{10}6s^1\). In order to study the nobility of gold Norskov et al. researched the reactivity towards hydrogen at the surface of different metals\(^3\). They concluded that the nobility of gold could be explained by two factors: the filling of the \(d\) band and the overlap between the orbitals of the metal and of hydrogen. When the electronic states of two atoms overlap, these should be orthogonal as required by the Pauli principle. This costs energy. However, there is also a gain in energy because the orbitals hybridize and form bonding and antibonding states. How much energy is gained depends on the filling of the \(d\)-band. More available electrons, thus a filled \(d\)-band, leads to the antibonding state being filled for gold much more than in for instance nickel and platinum. As the overlap between the \(s\)-band of hydrogen or another small atom and the \(d\)-band of the metal increases, the loss of energy due to orthogonalization increases as well. Since the \(5d\) state is more extended than the \(3d\) state, this overlap increases downwards in the periodic table, making it harder to adsorb hydrogen on gold than on copper. The combination of these factors lead to the conclusion that gold is the noblest of all metals. However, nanoscale clusters may behave very different from surfaces or bulk material. This mainly because the surface-to-volume ratio is much larger in clusters than in bulk, leading to a larger fraction of atoms which are incompletely bonded, for example.

The discovery of its different properties at nanoscale led to a flurry of research activity in this area. It is now known that not all gold clusters behave in the same way. Their catalytic activity is known to be very dependent of size, charge and support.

Even very small clusters, \(\text{Au}_2\)\(^4\) and \(\text{Au}_8\)\(^5\) are shown to display catalytic activity. In this regime, the size effect is very pronounced. Adding a single atom or electron changes the electronic structure drastically. Many properties of these clusters show a strong odd-even alternation. Negatively charged clusters with an even number of atoms are able to adsorb oxygen, for example, while odd-numbered clusters are not. This can be explained by their spin state. A gold atom has one unpaired electron, which means that odd-numbered gold anions have a closed shell. Thus it does not react with the electronegative oxygen, whereas the even-numbered anions with their free electron can bind to oxygen\(^6\). For neutral clusters, this reactivity towards oxygen is just the other way around, as expected according to the previous explanation. Not many data on neutral clusters are available, due to experimental difficulties.

In many experimental studies, gold clusters are deposited on a oxide surface. The nature of this support also influences the catalytic properties of gold\(^7\). In order to study the intrinsic properties of gold, free clusters in the gas phase are modeled in this work. This approach eliminates the influence of the support. As a size is chosen for the dimer, due to the limited amount of computational power needed. Further is chosen to model anions, to allow for comparison with experimental results\(^4\) and theoretical work by E. C. Beret for the neutral gold dimer\(^8\).

1.1.4 Towards design

In the past, catalysis research was largely a matter of trial and error. Finding a suitable catalyst was a matter of art as much as of science. When a material was found that catalyzed a reaction very well, it was not always clear why it worked. Since then, much progress has been made. With
the newest experimental techniques, it is possible to observe reactions even on very small scales. Computational methods have reached levels of accuracy which make it possible to explain and even predict properties of materials, including their potential for catalysis\cite{9}. It is now understood that catalysis cannot be seen as a static process, with the added bare material being the catalyst. Instead, catalysis is a dynamical process in which many structures and processes may play a role, dependent on the conditions of the environment. The state-of-the-art methods which are used in this work to gain more insight in the properties of Au$_2^-$ are explained in the next chapter.
2.1 Computational Physics

These days, properties of materials cannot only be discovered by measurements, but to some extent also theoretically. Computational methods have become invaluable in the design of new materials. While far from flawless, computational methods make it possible to predict properties before they are measured, thus offering some guidance for (costly) experiments. Of course the other direction is also possible: Computation might help to explain experimentally observed phenomena. It is possible to calculate preferred geometries, energies, bandgaps, vibrational modes and spectra for instance using computational methods.

For every calculation, a trade-off between accuracy and processing time needs to be considered. One way to describe interactions between atoms is with empirical potentials. These offer the benefit of speed, thus allowing the examination of large systems. Unfortunately, the use of empirical parameters means that a potential is specifically designed for one material, making the transferability poor. Furthermore there are not only transferability problems between different materials, but also for different properties. If potentials are optimized to find a certain property, it does not mean that they are suitable for finding another property. This stems from the way potentials are developed, with a subset of configurations with a known value for a certain property considered relevant for that property. These configurations do not need to be relevant for another property and the outcome of a calculation will be unpredictable.

A more rigorous way is to use \textit{ab initio}, or first principles, methods. The starting point of these methods is given by the Schrödinger equation. The many-body nature of this equation makes it impossible to solve analytically for all but the simplest systems. \textit{Ab initio} methods thus aim to solve the Schrödinger equation numerically. It is a challenge to find accurate approximations and develop a strategy to model materials at the atomic level. Although \textit{ab initio} methods are still approximations, they are free from empirical parameters. Another advantage is that their use is more general, where more empirical methods can be applied to specific systems only. The accuracy of \textit{ab initio} methods makes the results of calculations benchmark data when no experimental data are available.

The clusters considered in this work consist of only a few atoms, so computational speed is
CHAPTER 2. COMPUTATIONAL METHODS

less of an issue. Additionally, accuracy is required because the energy differences between isomers are small. This means that ab initio is the method of choice.

2.1.1 Different Ab Initio Methods

To simplify the Schrödinger equation, the first approximation used is the Born-Oppenheimer approximation. This treats the kinetic energy term of the nuclei as a perturbation. Since nuclei are so much heavier than electrons, this is in almost all cases a valid assumption. The Schrödinger equation is first solved for the unperturbed Hamiltonian. The wavefunctions of the perturbed Hamiltonian can now be written as a linear combination of the unperturbed states. This results in the factorization of the wave function into a nuclear and an electronic part.

One class of methods is based on the Hartree-Fock or self-consistent field approach. Here the wavefunction is split into single electron orbitals. These are used to iterate towards the lowest energy on the basis of the variational principle.

A different approach is to start from the electron density rather than the wavefunction. This is done in density functional theory, which is described in the next section.

2.2 Density Functional Theory

Density Functional Theory (DFT) is a widely used method within the field of computational physics since the 1970s. Here follows a short introduction. Many review articles and course materials on this subject are available for a much more in-depth approach, for example the introductory article ‘A Bird’s eye view of Density Functional Theory’,[10] Walter Kohn’s Nobel lecture[11] and the thorough review article ‘The density functional formalism, its applications and prospects’.[12]

As the name implies, Density Functional Theory uses the electron density as the basic variable. This idea was not new, Thomas and Fermi used it already in 1927 in their famous model. However, the Thomas-Fermi model is an approximation. The kinetic energy term is not exact. Additionally, electron exchange and correlation are neglected. This leads to inaccurate results. Molecular bonding for example cannot be explained by the Thomas-Fermi approximation, in which the energy of separate atoms is always lower than that of a molecule. In the sixties a more rigorous approach followed when Hohenberg and Kohn introduced two theorems, providing the starting point for DFT.

The first Hohenberg Kohn theorem states that the charge density uniquely determines the external potential. The proof of this is elegant and simple: suppose there are two different potentials. These two external potentials would lead to two different Hamiltonians, $H^1$ and $H^2$, which have different ground state wave functions, $\Psi^1$ and $\Psi^2$. From the variational principle follows

$$E^1 = \langle \Psi^1 | H^1 | \Psi^1 \rangle \leq \langle \Psi^2 | H^1 | \Psi^2 \rangle$$

and using

$$H^1 = H^2 - V^2_{\text{ext}} + V^1_{\text{ext}}$$

gives

$$E^1 < E^2 + \int d^3r V^1_{\text{ext}} - V^2_{\text{ext}}$$
2.2. DENSITY FUNCTIONAL THEORY

The same reasoning could be followed starting from $E^2$, exchanging signs. This gives

$$E^2 < E^1 + \int d^3r V^2_{\text{ext}} - V^1_{\text{ext}}$$

which is a contradiction, unless $V^2_{\text{ext}} = V^1_{\text{ext}}$. Thus, the ground state density gives a unique potential, which leads to the wave function and all other observables.

Unfortunately, although this proves that there is not more than one potential corresponding to a density, it does not prove that there is one. That is, there could also be zero potentials. This problem is known as V-representability and gives restraints on the class of densities that can be used.

Working with the charge density instead of the wave function simplifies the problem by reducing the number of degrees of freedom from $3N$ to 3. This greatly improves the scalability, one of major problems in computational physics. Calculations become more expensive very quickly as the system size grows. DFT scales better than other methods and can therefore also be used for larger systems.

Furthermore, the charge density is much easier to imagine than something as abstract as the wave function. This theorem is only valid for the charge density of the ground state and is not applicable to excited states. This is one of the limitations of DFT.

Additionally, a variational principle for the density can be derived:

$$E_n[n_0] \leq E_n[n'] = F[n'] + \int V_{\text{ext}}n'(r)dr$$

where $V_{\text{ext}}$ is the external potential and $F$ is a functional of the density. A functional ($F[n]$) converts a function ($n$) into a number, just like a function $f(x)$ converts a number ($x$) in a number. The universal part of the energy is given by the functional

$$F[n'] = \langle \Psi | T + V_{e-e} | \Psi \rangle$$

where $T$ is the kinetic energy operator and $V_{e-e}$ is the electron-electron interaction operator. The system-dependent part is contained in the external potential $V_{\text{ext}}$. This variational principle says that the energy obtained from the ground state density $n_0$ is always lower or equal to the energy obtained from any arbitrary density $n'$, also called trial density. This is known as the second Hohenberg Kohn theorem.

Kohn and Sham further refined this approach. They proposed to split the functional $F[n']$ into different terms:

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$

which extracts two large and easy to calculate terms from the equation. The kinetic energy term $T_s$ is not the actual kinetic energy of the system, but the energy of the non-interacting problem. The expression for the potential energy or Hartree Energy,

$$E_H[n'] = \frac{1}{2} \int \frac{n'(r) - n'(r')}{|r - r'|} dr$$

stems from the mean field potential. The part which is left is the exchange-correlation term and contains the interactions between electrons. It is the only approximation in this equation. If $E_{xc}$ were exact, all many-body interactions would be included.

The variational principle can be rewritten as

$$E[n'(r)] = \int V_{\text{ext}}n'(r)dr + T_s[n'(r)] + E_H[n'] + E_{xc}[n'] \leq E$$
By using the Euler-Lagrange equation and the fact that the number of electrons is constant, a set of self-consistent equations can be obtained.

\[ h_{KS} \psi_j = \left( \frac{1}{2} \nabla^2 + v_{eff}(r) \right) \psi_j = \epsilon_j \psi_j \]

\[ n(r) = \sum_{j=1}^{N} |\psi_j(r)| \]

\[ v_{eff}(r) = v(r) + \int \frac{n(r')}{|r - r'|} dr' + v_{xc}(r) \]

These are called the Kohn-Sham equations. The fact that they are self-consistent means that the Kohn-Sham Hamiltonian, \( h_{KS} \), depends on its own solution. Thus, the solution is found when the eigenfunctions of the Hamiltonian give a charge density that leads to the same Hamiltonian.

The accuracy of methods using these equations depends on the exchange-correlation functional. Although this term is small, it is essential to describe the chemistry of the system. Different functionals are used for the exchange correlation function, and again the balance between desired accuracy and computer time has to be found. The simplest of exchange correlation functionals is the local-density approximation (LDA). Here the xc-functional depends only on the density of the point where it is evaluated, hence local. Although this is a crude approximation, for some properties it gives surprisingly accurate results. Generalized gradient approximations (GGA) also take the gradient of the density into account. A widely used GGA xc-functional is the Perdew-Burke-Ernzerhof functional\(^{[13]}\).

### 2.3 The code FHI Aims

Since the Kohn-Sham equations are self-consistent, they need to be solved in an iterative way. This approach translates in a method:

1. Guess an initial charge density
2. Obtain the potential for this density
3. Calculate the eigenvalues and wavefunctions / solve KS equations
4. Calculate new charge density

in which the third step is the expensive one. This cycle terminates when the initial and the new charge density are equal within a given level of accuracy. Then, self-consistency is reached. Many codes are available to perform these DFT calculations. In this work, FHI-aims\(^{[14]}\) is used, which stands for Fritz Haber Institute ab initio molecular simulations.

In order to allow a numerical solution, the Kohn-Sham orbitals are expanded as

\[ \Psi_l(r) = \sum_{i=1}^{N_b} \phi_i \]

which is a linear combination of basis functions, \( \phi_i \). All basis functions \( \phi_i \) together form the basis set. This is used to turn the Kohn Sham equations into an eigenvalue problem

\[ \sum_j h_{ij} c_j = \epsilon_l \sum_j s_{ij} c_j \]

which can be solved numerically.
2.3. THE CODE FHI AIMS

2.3.1 The basis set

The accuracy of the calculation depends on the basis set. As a basis set is more complete, better approximations of $\phi_i$ can be made, thus increasing the accuracy at the cost of computational speed. Since the desired degree of accuracy differs, there should be different basis sets available, starting from a minimal basis up to very high accuracy.

In FHI-aims, the basis functions are chosen to be numeric atom-centered orbitals of the form:

$$\phi_i(r) = \frac{u_i(r)}{r} Y_{lm}$$

where $u_i(r)$ is the numerically tabulated part. Numerically tabulating this part makes the basis functions very flexible and allows to create the basis set as compact as possible. To prevent slowing down of the calculations by irrelevant tails of the function a confining potential is added.

The minimal basis set in FHI-aims is composed of numerical solutions of a Schrödinger-like equation for spherically symmetric free atoms. It is desirable for bigger basis sets contain all smaller ones to guarantee convergence. Bigger basis sets in FHI-aims are made by starting from a smaller basis set and expanding these by addition of basis functions from a large pool of functions. The function is selected on the basis of improvement in energy: each basis function was added in turn and the one which offered the largest decrease in energy was added to the set. This approach avoids human bias. FHI-aims contains basis sets created this way for almost all atoms in the periodic table.

2.3.2 Relativistic effects

Near the heavy nuclei of gold, electrons can move at a significant fraction of the speed of light. For gold, also valence electrons are influenced by relativity due to the electronic structure. This means that a relativistic correction needs to be added to the kinetic energy. This is done using the atomic zeroth order regular approximation (ZORA)\textsuperscript{[15]}. The kinetic energy operator now becomes

$$T_{ZORA} = \frac{p \cdot \mathbf{c}^2}{2c^2 - v_{\text{free}}^2} \cdot p$$

where $v_{\text{free}}$ is the free-atom potential at the atomic center. This correction has significant effect on the binding energy and bondlength of the gold dimer, which decrease with more than 0.8 eV and 0.2 Å\textsuperscript{[14]}, respectively.

2.3.3 Van der Waals forces

Although dispersion interactions play a noticeable role in the description of gold clusters, it is not expected to alter the structures of clusters as small as a dimer for the simple reason that different structures are not possible. Van der Waals forces have been documented to have a large effect for larger clusters\textsuperscript{[8]} and may also have an effect on the clusters with many ligands sampled in this work. Due to this and to ensure a homogeneous treatment within the group, van der Waals forces have been included in the calculations. The potential between two polarizable systems is expressed as

$$V = -C_6/R^6 + O(1/R^8)$$
and this is included by adding a $C_6[n]/r^6$ tail correction to the PBE energy, where the $C_6[n]$ coefficients are derived from the self-consistent electron density $n$.\[10]

## 2.4 Basin Hopping

In order to find the isomer with the lowest energy of a certain composition, a thorough exploration of the phase space is necessary. Drawing structures and optimizing them is not enough, structures can easily be missed, especially when clusters are a bit bigger. What is needed then, is a method to scan the phase space in an unbiased way. This is provided by basin hopping\[17] as implemented in FHI-Aims\[18].

In basin hopping, a certain geometry is optimized. Next, this optimized geometry is perturbed randomly. One or all atoms are scrambled within certain conditions. Atoms cannot be too close to another, for example. An optimization follows, which leads either to the same or another minimum. A trial move may also be rejected if the newly found minimum is too high in energy. In that case, the previous minimum will be the starting geometry for the next trial move. The found minima are ordered with respect to energy and their geometries are used for optimization at higher accuracy. For small clusters, this is very efficient.

Unfortunately, no matter how good the sampling method is, there is no way to be sure if all isomers have been found. Any missed structure may be the most stable configuration. An indication of completeness is given by the results of different sampling runs; if basin hopping with very different starting geometries returns similar structures, this is a fair indication that the sampling is complete. However, it is still possible that a basin for a certain isomer is very narrow, which means that the geometry to be optimized needs to be very close to the geometry of that isomer. This is often the case for linear structures, which is easily solved by using linear configurations as starting geometries. In other cases, no solution has been found. This becomes a problem especially as the number of oxygen atoms increases. Many structures containing molecular oxygen separate from the cluster are typically found. However, basin hopping is still a major improvement when comparing to manually drawing structures. Many new minima have been found.

Results could maybe improve if some adaptations to the method are made. One could think of keeping the CO bond intact, since this bond is never broken. There might also be a way to decrease the number of structures containing separate oxygen molecules found by basin hopping, by analysing the found minima also on bond lengths. However, problems remain and for larger gold clusters another sampling method may be necessary.

## 2.5 Ab Initio Atomistic Thermodynamics

### 2.5.1 Temperature

Thus far, temperature is not taken into account. As the effects of temperature at the free energy are not at all negligible, it is necessary to include these contributions and contributions from the pressures of the reacting gases. This is done using *ab initio atomistic thermodynamics*\[19]\[20]\[21]\[22]. The Gibbs free energy may be obtained from the partition function in the canonical ensemble:

$$G = -k_BT \ln q$$
The partition function $q$ of a molecule can be factorized into the translational, rotational, configurational, vibrational, electronic and nuclear contributions:

$$q = q^{tr} q^{rot} q^{conf} q^{vib} q^{el} q^{nuc}$$

A molecule with $N$ atoms has $3N$ degrees of freedom. Three of those are translational, three are rotational and the remaining $3N-6$ are vibrational for non-linear molecules. Linear molecules have two rotational degrees of freedom and $3N-5$ vibrational degrees of freedom.

**Electronic**

The electronic levels are generally widely separated in comparison to $k_B T$. Thus we only consider the lowest level

$$q^{el} = \sum_i (\nu_i e^{E_i/k_B T}) = v_0 e^{E_0/k_B T}$$

where $E_0$ is the energy obtained from the DFT calculations. The term $v_0$ is the degeneracy of the ground state, equal to the spin multiplicity.

**Vibrational**

Vibrational motion is relative motion of two atoms within the cluster. This can be described with the harmonic oscillator approximation. For a diatomic molecule and a single vibrational mode, the energy levels are

$$\epsilon = (n + \frac{1}{2}) \hbar \nu$$

where $n$ is an integer and $\nu$ the eigenfrequency of the vibrational mode.

The partition function is thus:

$$q^{vib} = e^{\hbar \nu/2k_B T} \sum_{n=0}^{\infty} e^{n\hbar \nu/k_B T}$$

which can be evaluated analytically to

$$q^{vib} = e^{\hbar \nu/2k_B T} \frac{1}{1 - e^{\hbar \nu/k_B T}}$$

The extension to the partition function of a larger molecule is a straightforward multiplication over all the vibrational levels:

$$q^{vib} = \prod_i \left[ e^{-\frac{\hbar \nu_i}{2k_B T}} (1 - e^{-\frac{\hbar \nu_i}{k_B T}}) \right]$$

where $\nu_i$ are the vibrational frequencies of the molecule. These are calculated in a part of FHI-aims for vibrational analysis. First, the Hessian matrix at the equilibrium positions of the atoms,

$$H_{i,j} = \left( \frac{\partial^2 V}{\partial \xi_i \xi_j} \right)_0$$

is extracted. A Hessian is a matrix which contains the second derivatives of a function, in this case the second derivative of the potential $V$ with respect to the displacements in cartesian
coordinates. In our implementation, the first derivative is calculated analytically but the next derivative is numerical. The Hessian is converted to mass weighted cartesian coordinates and diagonalized, yielding $3N$ eigenvectors and $3N$ eigenvalues. The eigenvalues are the squares of the frequencies of the molecules. Then, it is determined which frequencies belong to the rotational and translational degrees of freedom.

**Rotational**

For the derivation of the partition function for the rotational motion, the rigid rotor approximation is used, implying that the distance between the atoms does not change during rotation.

To compute the energy associated with rotation, first coordinate system is shifted to one with the origin on the center of mass. Next, the moments of inertia are calculated

$$I = \sum_{i=1}^{N} M_i R_i^2$$

For an asymmetrical rotor in the classical limit ($T \gg \Theta$)

$$q^{\text{rot}} = 8\pi^2 \left(\frac{2\pi k_B T}{\hbar^2}\right)^{3/2} (I_A I_B I_C)^{1/2}$$

and $\Theta = 2 \cdot 10^{-1} K$ for a gold dimer anion, so the system is safely in the classical limit. For a linear moment, the partition function is

$$q^{\text{rot}} = \frac{8\pi^2 I_A k_B T}{\hbar^2}.$$ 

The rotational energy thus only depends on mass and geometry of the molecule. Since mass is an inherent property and the optimized geometry is the output of a DFT calculation, finding the rotational energy computationally is straightforward.

**Translational**

Translational motion is the motion of the entire particle through space, without changing the orientation of the particle or the particle itself. The particle-in-a-box model can be used for the motion of a particle in a confined space. The energy levels of a particle in a three dimensional box are well known from quantum mechanics:

$$\epsilon_{n_x n_y n_z} = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2).$$

where $n_x$, $n_y$ and $n_z$ are integers. Since these energy levels are closely together compared to $k_B T$, the summation in the partition function can be replaced by an integral:

$$q^{tr} = \left[\int_0^{\infty} e^{\frac{\hbar^2 n^2}{8mL^2}} \right]^3 = \left(\frac{2\pi mkT}{\hbar^2}\right)^{3/2} V$$

in which the volume is a reference volume. If clusters are compared, the volume contribution in both clusters cancels. When a comparison is made between a ligand adsorbed on a cluster with cluster and the ligand in gas form, this is not possible. However, the volume contribution can be
rewritten in terms of pressure using the ideal gas approximation, which assumes non-interacting particles. Using this approximation, the translational partition function is rewritten as

\[ q^{tr} = \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} \frac{k_B T}{p} \]

which can be used for the calculation of the chemical potential \( \mu \) of the ligand gases.

**Configurational**

Whereas vibrational and translational motion are independent of the atoms of which the molecule consists, rotation is not. Rotating a diatomic molecule with two identical nuclei by 180 degrees, brings the molecule back in its original position. To avoid double counting these isomers, a configurational term needs to be introduced in the partition function:

\[ q^{conf} = \frac{1}{\sigma} \]

where \( \sigma \) is the number of indistinguishable configurations.

### 2.5.2 Pressure

In modeling a realistic environment, not only temperature but also pressures of the reactant gases should be taken into account. This is expressed in the free energy of formation

\[ \Delta G = G_{\text{cluster} + \text{ligand}}(T) - G_{\text{cluster}}(T) - \mu_{\text{ligand}}(T, p) \]  

(2.1)

where the free energy of the isomer is compared to the free energies of its parts. Which composition is energetically most favourable thus depends on the amount of ligands present.

### 2.6 Molecular Dynamics

The dynamical properties of a system can be studied using Molecular Dynamics. The classical equations of motion are integrated to study the time evolution of the system. Using the classical approximation is allowed as long as the de Broglie wavelength is much smaller than the distances between the atoms. At room temperature, this is the case for all but the lightest molecules.

Every timestep the atoms are moved according to Newtons equations of motion, using the positions and velocities of the atoms and the acceleration from the forces on the atoms. Although this is classical, the entire method is not. The forces can be calculated using either an empirical potential or use \textit{ab initio} calculations. The latter, First Principles Molecular Dynamics is used here.

When the atoms move according to the laws of classical mechanics, the total energy is constant. Kinetic energy can be transformed into potential energy and the other way around. The simulation is a way to sample the microcanonical ensemble, where number of particles, volume and total energy are kept constant. The total energy can be monitored and provides a way to check the parameters of the simulation. If the energy fluctuates too much or drifts away, the timestep may be too large.
The temperature in a molecular dynamics simulation can be obtained from the equipartition theory, which says that every degree of freedom contributes $\frac{1}{2}k_B T$ to the kinetic energy. This leads to the following expression for temperature

$$T(t) = \sum_{i=1}^{N} \frac{m_i v_i^2}{k_B N_f}$$

where $N_f$ is the number of degrees of freedom. For a three dimensional system with fixed momentum, $N_f$ is equal to $3N - 3$ where $N$ is the number of particles. It is also possible to sample the canonical ensemble, that is, keep temperature instead of energy constant. This can be done by rescaling the velocities of the atoms after each timestep in order to keep the canonical distribution using a thermostat. Preferably, this should be done without introducing discontinuities. It is also desirable to have a conserved quantity analogous to the energy in the microcanonical ensemble. The conservation of this quantity gives an index of the reliability of the thermostat. The Bussi-Donadio-Parrinello thermostat\cite{23} can do this.

In this thermostat the rescaling of the velocities is downsized by a parameter $\tau^{-1}$, so the rescaling is smoother. To realize this, the target kinetic energy is obtained from the previous kinetic energy, with the constraint that the canonical distribution should remain unchanged.

This approach leads to the conservation of a Hamiltonian with an extra term:

$$H'(t) = H(t) - \int_{0}^{t} (\bar{K} - K(t')) \frac{dt'}{\tau} - 2 \int_{0}^{t} \sqrt{\frac{K(t') - K}{N_f}} \frac{dW(t')}{\sqrt{\tau}}$$

where $K$ is the kinetic energy, $\bar{K}$ is the average kinetic energy, $\tau$ is a parameter with units of time, $N_f$ is the number of degrees of freedom of the system and $dW$ is Wiener noise. The physical interpretation of this Hamiltonian is that the flux of energy between the thermostat and the system. This provides a way to check the performance of the thermostat. Other than the conserved energy in the microcanonical ensemble, the value of $\tilde{H}$ has no physical meaning but is dependent on the parameters of the simulation.

The MD simulation using this thermostat requires two input variables: the timestep and the parameter $\tau$, which acts as a relaxation time. If the conserved quantity $\tilde{H}$ fluctuates too much, these variables need to be changed. One of the advantages of the Bussi-Donadio-Parrinello thermostat is that, compared to other thermostats, it is relatively independent of the variable $\tau$. 

\[14\]
Results: adsorption of $O_2$ and CO on $Au_2^-$

In this chapter, the results of the sampling and analysis of the gold dimer anion with oxygen and carbon monoxide ligands are presented. Compositions of the form $Au_2O_xCO_y^-$ are sampled, with $x \in [0, 8]$ and $y \in [0, 4]$ and for several spin states. This way, over 200 local minima were found. The geometries correspond well with structures found previously in other studies\cite{24}\cite{25}, but new geometries are also found. Several structural motives are shared between different compositions, illustrated below. Their relative energies of formation are compared using ab initio atomistic thermodynamics, see section 3.2.

3.1 Ligand Adsorption

3.1.1 Adsorption of atomic and molecular oxygen

Oxygen can bind to $Au_2^-$ in many ways, adsorbing dissociated or molecular, forming a triangle with the gold dimer or forming chains of oxygen atoms. The most stable configurations of each composition are shown in table 3.1. For comparison some isomers where oxygen is bound in another form are also given.

The binding energy is defined as

$$E_b = -E(Au_2O_x^-) + E(Au_2^-) + \frac{x}{2}E(O_2)$$

and for comparison, the binding energy per oxygen atom is also given per oxygen atom.

Some geometries are stabilized much more than others. This effect is clearly seen in the binding energy for an extra oxygen atom

$$E'_b = -E(Au_2O_x^-) + E(Au_2O_{x-1}^-) + \frac{1}{2}E(O_2)$$

in table 3.1. These energies differ considerably. It is very favourable to adsorb a third oxygen atom, for example. This leads to a chain of alternated oxygen and gold atom, a structural type which is also found to be very favourable in experiments on $Au_nO_x^-\cite{25}$.
Table 3.1: Binding of Au$_2^-$ with oxygen. Above the line are the most energetically favourable isomers. Below the line are isomers with oxygen bound in a different way, for comparison.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>Multiplicity (2S+1)</th>
<th>$E_b$ (eV)</th>
<th>$E'_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_2$O$^-$</td>
<td>2</td>
<td>0.66</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>Au$_2$O$_2^-$</td>
<td>2</td>
<td>1.42</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>Au$_2$O$_3^-$</td>
<td>4</td>
<td>2.48</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>Au$_2$O$_4^-$</td>
<td>4</td>
<td>2.79</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Au$_2$O$_5^-$</td>
<td>4</td>
<td>2.98</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Au$_2$O$_2^-$</td>
<td>2</td>
<td>1.37</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>Au$_2$O$_3^-$</td>
<td>2</td>
<td>1.59</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Au$_2$O$_4^-$</td>
<td>4</td>
<td>2.12</td>
<td>-0.36</td>
<td></td>
</tr>
</tbody>
</table>
3.2. PHASE DIAGRAMS

Table 3.2: Binding of $\text{Au}_2^-$ with carbon monoxide

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>Multiplicity (2S+1)</th>
<th>$E_b$ (eV)</th>
<th>$E'_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}_2\text{CO}^-$</td>
<td>2</td>
<td>1.07</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>$\text{Au}_2(\text{CO})_2^-$</td>
<td>2</td>
<td>2.03</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>$\text{Au}_2(\text{CO})_3^-$</td>
<td>2</td>
<td>2.68</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>$\text{Au}_2(\text{CO})_4^-$</td>
<td>2</td>
<td>3.38</td>
<td>0.70</td>
<td></td>
</tr>
</tbody>
</table>

3.1.2 Adsorption of carbon monoxide

The binding of $\text{Au}_2^-$ to carbon monoxide is more predictable than the binding to oxygen. The most stable configurations of the form $\text{Au}_2(\text{CO})_y^-$ are formed when the carbon atom of carbon monoxide is bound to a single gold atom, see table 3.2.

Binding of an extra CO ligand is in general less favourable than the previous addition of a CO ligand, with the exception of the fourth ligand. Addition of this leads to a very symmetric geometry. As in the case of oxygen, which composition is the most stable is dependent on the temperature and pressure of the reacting gas.

3.1.3 Coadsorption

The most interesting from a catalysis point of view are the structures were O and CO are both adsorbed. The sampling shows that in almost all cases, structures of the form $\text{R–CO}_2$ or $\text{R–CO}_3$ are preferred to structures were O and CO are adsorbed on different ends of the dimer. To see whether these structures are also preferred to structures with only one type of ligand, the free energies of formation are compared and visualized in a phase diagram.

3.2 Phase Diagrams

For this system, the free energy of formation is given by

$$\Delta G_f = G_{\text{Au}_2\text{O}_x(\text{CO})_y}(T) - G_{\text{Au}_2}(T) - \frac{x}{2} \mu_{\text{O}_2}(T, p) - y \mu_{\text{CO}}(T, p)$$  \hspace{1cm} (3.1)

and depends on the temperature and the pressure of oxygen and carbon monoxide. These gases are considered to be in equilibrium with the clusters, but not with each other. This is treated in more detail in section 3.3. If oxygen pressure is high, the equilibrium shifts toward adsorption on the cluster. If oxygen pressure is low, the gain in electronic energy can no longer compensate for the loss of translational energy. Then, it is more favourable to move around freely instead of adsorbing on the cluster.
This can be shown as a plane in the three dimensional $\mu_{O_2}$, $\mu_{CO}$, $\Delta G$ space, as shown in figure 3.1.

![Figure 3.1: Three dimensional phase diagram obtained for Au$_2$O$_x$CO$_y^-$ clusters at 300 K. Every colour represents a different composition.](image)

Since the prime interest is in the most thermodynamically favourable isomer, or the lowest lying plane, a projection showing only the lowest lying isomer as a function of $\mu_{O_2}$ and $\mu_{CO}$ is made. This is called a phase diagram. The favoured compositions in different environmental conditions are visible as coloured regions in the phase diagram.

In figure 3.2, a phase diagram for clusters of the composition Au$_2$O$_x$CO$_y^-$ is shown. This figure shows the isomer with the lowest energy of formation at 300 K for a wide range of pressures. In the lower left part of the diagram, where CO and O$_2$ pressure are very low, the bare cluster is the most favourable state. It is interesting that oxygen adsorption does not increase linearly with increasing oxygen pressure, but instead there is a transition from the bare cluster to Au$_2$O$_3^-$, Au$_2$O$_4^-$ and Au$_2$O$_5^-$. This could also be seen in table 3.1, the adsorption of an extra oxygen atom to form Au$_2$O$_3^-$ is paired with a large gain in energy, see table 3.1. Even with very little oxygen present, Au$_2$OCO$^-$ and Au$_2$O$_2$CO$_2^-$ are found to be the most energetically favourable compositions at increasing CO pressure. This can be explained by the formation of a adsorbed CO$_2$. Structures of the form R–CO$_2$ and R–CO$_3$ are also found further up and to right in the diagram. The most thermodynamically favourable isomer around ambient conditions contains both CO$_2$ and CO$_3$ adsorbates.

### 3.3 Desorption of CO$_2$

Thus far, the formation of CO$_2$ is neglected. The system is considered to be in constrained equilibrium; the clusters are in equilibrium with O$_2$ and CO, but those are not in equilibrium with each other. That this reaction does not occur spontaneously is a realistic assumption; the barriers are too high or the reaction is spin-forbidden. However, this way the clusters are also not in equilibrium with CO$_2$. Because many favourable isomers are of the form R–CO$_2$ or R–CO$_3$, ...
3.3. DESORPTION OF CO₂

Figure 3.2: Phase diagram obtained for Au₂OₓCOᵧ⁻ clusters at 300 K. Every colour represents a different composition, which is the most energetically favourable under the environmental conditions in that region.

It is plausible that they are able to desorb CO₂. We consider the reaction

\[ R - CO₂ \rightleftharpoons R + CO₂(g) \]

and aim to find the pressure of CO₂ where this is an equilibrium, \( p_{CO₂}^{eq} \). This is done by treating CO₂ similar to the other gases and calculating the free energy of formation:

\[ \Delta G = G(R - CO₂) - G(R) - \mu_{CO₂} \]

where \( \mu \) has a term explicitly dependent on pressure, from the translational contribution:

\[ \mu_{CO₂} = \mu'_{CO₂} + kT \ln(p_{CO₂}) \]

where \( \mu'_{CO₂} \) contains all terms contributing to \( \mu \) except the pressure term. Next, the equilibrium pressure \( p_{CO₂}^{eq} \) is calculated from

\[ G(R - CO₂) - G(R) - \mu'_{CO₂} - kT \ln(p_{CO₂}^{eq}) = 0 \]

If the CO₂ pressure in the environment is below this equilibrium pressure it is favourable to desorb CO₂, while at pressures above the equilibrium pressure it is favourable to remain adsorbed on the cluster.

The calculated equilibrium pressures are shown in table 3.3. Which isomers dissociate depends on experimental conditions. The CO₂ pressure in the atmosphere is approximately 10⁻³ atm. In ion trap experiments [4], O₂ and CO pressures are around 10⁻⁶ atm, so the CO₂ pressure should be lower. In those conditions, Au₂O₂(CO)⁺, will not desorb CO₂. The most thermodynamically favourable structure, Au₂O₄(CO)₂⁻ is a border case.

When considering only thermodynamics, this would lead to the conclusion that every gold dimer would form Au₂O₄(CO)₂⁻ at equilibrium, from where it would not react further. This
CHAPTER 3. RESULTS: ADSORPTION OF O₂ AND CO ON AU₂⁻

<table>
<thead>
<tr>
<th>R–CO₂</th>
<th>R</th>
<th>∆G_f (eV)</th>
<th>p_{CO₂}^e0 (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au₂O₄(CO)₂⁻</td>
<td>Au₂O₃⁻</td>
<td>−5.01</td>
<td>3 E−07</td>
</tr>
<tr>
<td>Au₂O₃(CO)₂⁻</td>
<td>Au₂O₂⁻</td>
<td>−4.24</td>
<td>3 E+16</td>
</tr>
<tr>
<td>Au₂O₂(CO)₂⁻</td>
<td>Au₂O⁻</td>
<td>−4.18</td>
<td>3 E+01</td>
</tr>
<tr>
<td>Au₂O₂CO⁻</td>
<td>Au₂O⁻</td>
<td>−3.21</td>
<td>3 E−18</td>
</tr>
<tr>
<td>Au₂O₂(CO)₃⁻</td>
<td>Au₂O(CO)₂⁻</td>
<td>−3.05</td>
<td>5 E+01</td>
</tr>
<tr>
<td>Au₂O₄⁻</td>
<td>Au₂O₂⁻</td>
<td>−2.60</td>
<td>2 E−03</td>
</tr>
<tr>
<td>Au₂O₄CO⁻</td>
<td>Au₂O₃⁻</td>
<td>−2.39</td>
<td>5 E−05</td>
</tr>
<tr>
<td>Au₂O₃(CO)₃⁻</td>
<td>Au₂(CO)₂⁻</td>
<td>−2.27</td>
<td>4 E+11</td>
</tr>
</tbody>
</table>

Table 3.3: CO₂ equilibrium pressures for several isomers. ∆G_f is given for T = 300K, p_{CO} = 10⁻⁶ and p_{O₂} = 10⁻⁶, shown as a star in the phase diagram in figure 3.3.

would mean that the catalyst would be poisoned at CO₂ pressures higher than 3·10⁻⁷ atm. However, whether this isomer is formed can be debated. This is treated in more detail in section 3.5.

When the isomers which dissociate CO₂ at pressures p_{CO₂} > 10⁻⁸ atm are removed from the phase diagram, the picture changes completely, see figure 3.3. The previous phase diagram (fig. 3.2) may be regarded as the phase diagram at infinite CO₂ pressure. Since CO₂ is treated analogously to the gases O₂ and CO, the CO₂ axis can be viewed in the same way as the O₂ and CO axis. Projections with the isomers with the lowest free energy of formation can be made with a fixed value for one of the three gases and the other two gases on the axes. In figure 3.3 p_{CO₂} is fixed at 10⁻⁸ atm, while in figure 3.2 p_{CO₂} = ∞. The structures in the latter are the thermodynamically most favourable but not stable and can thus be considered to be reaction intermediates.

The structures that appear in figure 3.3 are the most energetically favourable ones which are stable with respect towards CO, O₂ and CO₂. For Au₂, this is not the pristine cluster but Au₂O₂CO⁻. Further adsorption of O₂ and CO would lead to structures which desorb CO₂, after which Au₂O₂CO⁻ would be regenerated. This means that Au₂O₂CO⁻ should be regarded as the catalyst and not the pristine cluster Au₂⁻!

3.4 The effect of temperature

The free energy of structures depends on temperature. It is thus no surprise that the phase diagrams at 100 K and 600 K look different from the ones at 300 K, see figure 3.4 and figure 3.5. The trends are obvious: at 100 K adsorption is more favourable, making Au₂O₄(CO)₂⁻ the only visible isomer. This also means that it is harder to dissociate CO₂. At 100 K, the equilibrium pressure for Au₂O₄CO₂⁻ is 6·10⁻²⁹ atm. Thus, the phase diagram remains unchanged at all reasonable CO₂ conditions.

At a temperature of 600 K, the cluster without ligands occupies a larger fraction of the phase diagram, see figure 3.5. This illustrates that ligand adsorption is less favourable at higher temperatures. When cluster and ligand each move and rotate independently, their combined translational and rotational energy are larger than a cluster with an adsorbed ligand. At higher temperatures, this gain in translational and rotational energy is larger which means that adsorption is less favoured. This also shows in the dissociation of CO₂. At 600 K, Au₂O₂CO⁻
3.5 TOWARDS A REACTION PATH

It is clear now that there is competition between different structures. There is a thermodynamic drive towards the reaction intermediate, but this is not a stable structure and will dissociate CO₂. This leads then towards the catalyst, which is stable but in an environment of CO and O₂ not the most energetically favourable.

The next step is to construct a pathway which connects the proposed catalyst and reaction intermediate. Additionally, there should be a way for Au₂⁻ to enter this circle. After all, this is the material which is introduced in the reactor.

This reaction path should also conserve spin. For this system, this is not such a big constraint, because Au₂⁻ is a doublet. Upon adsorption of CO it will remain a doublet and upon adsorption an O₂ molecule it will either remain a doublet or become a quadruplet. The structure will keep the same spin state when it desorbs CO₂, since this is a singlet. Only Au₂O₃⁻, Au₂O₄⁻ and Au₂O₅⁻ have a quadruplet as the most stable structure. For all other compositions a doublet is the preferred state. The isomers in the reaction path in figure 3.7 are all doublets.

Figure 3.3: Phase diagram obtained for Au₂OₓCOₙ⁻ clusters at 300 K at pCO₂ = 10⁻⁸ atm. Each region shows the preferred composition under the corresponding O₂ and CO pressures.

dissociates at pCO₂ = 4 · 10⁻¹ atm. Below this pressure all isomers dissociate CO₂. This is relevant, since the clusters gain energy upon adsorption of ligands and are until thermalization hotter than their environment. It is not possible to predict timescales using only thermodynamics. However, this finding raises the question whether larger isomers, for example Au₂O₄CO₂⁻ can be formed. Formation of this isomer requires four consecutive adsorptions, without desorbing CO₂ in the mean time. The desorption of CO₂ from Au₂O₂CO₂⁻, a possible precursor of Au₂O₄CO₂⁻, is paired with a gain in free energy. It may be possible to overcome barriers because the energy gained upon previous adsorption of ligands is, before thermalization, still in the cluster. Whether this is likely to happen before an O₂ molecule is adsorbed should be answered in a kinetic study.
CHAPTER 3. RESULTS: ADSORPTION OF O\textsubscript{2} AND CO ON AU\textsubscript{2}−

Figure 3.4: Phase diagram obtained for Au\textsubscript{2}O\textsubscript{x}CO\textsubscript{y}− clusters at 100 K at infinite CO\textsubscript{2} pressure. Each region shows the preferred composition under the corresponding O\textsubscript{2} and CO pressures.

Figure 3.5: Phase diagram obtained for Au\textsubscript{2}O\textsubscript{x}CO\textsubscript{y}− clusters at 600 K at pCO\textsubscript{2} = ∞. Each region shows the preferred composition under the corresponding O\textsubscript{2} and CO pressures.
Figure 3.6: Phase diagram obtained for $\text{Au}_2\text{O}_x\text{CO}_y^-$ clusters at 600 K at $p_{\text{CO}_2} < 10^{-1}$ atm. Each region shows the preferred composition under the corresponding $O_2$ and CO pressures.

To obtain such a reaction path connecting catalyst and reaction intermediate and conserving spin, we looked at differences in free energy ($\Delta G$) at different temperatures and pressures. Many different pathways are possible. An example pathway was started at $\text{Au}_2\text{O}_2\text{CO}^-$, our proposed catalyst. At every step, the three available reactions – adsorption of CO or $O_2$ or desorption of $\text{CO}_2$ – were compared and the most thermodynamically favourable reaction was added to the reaction path. This led to the pathway depicted by a solid line in figure 3.7, a cycle connecting catalyst and reaction intermediate. The differences in energy are given in table 3.5.

The free energies in table 3.5 are based on low-pressure conditions, $p_{O_2} = 10^{-6}$ atm, $p_{\text{CO}} = 10^{-6}$ atm, $p_{\text{CO}_2} = 10^{-8}$ atm. Additionally, the differences are given at 0 K, $E^{DFT}$. These energies are the differences in energy for the most stable configuration of each composition. The most likely reaction path is not determined by thermodynamics alone. One needs to study kinetics to determine timescales and barriers of reactions and thus predict which reactions are likely to happen. Several questions which need to be answered by a kinetic study are addressed below.

First, there are often several reactions which lead to a gain in free energy possible. The reaction with the largest gain in energy does not need to be the most likely reaction to occur. It might, for instance, require collision with a ligand. At low pressures this could take a long time. Before that happens, the cluster might have desorbed CO$_2$. Also, there might be a large gain in energy upon adsorption or desorption, but a high energy barrier could prevent this reaction from happening. Additionally, upon adsorption of a ligand, the clusters are for a short time hotter than their environment. In this excited state it could be easier to desorb CO$_2$. With the extra energy in the cluster it is possible to overcome barriers preventing desorption. Furthermore, only the most stable geometries of a certain composition are taken into account. Upon adsorption of a ligand a different, less favoured geometry, a local minimum, may be formed. From this geometry, it could be favourable to desorb CO$_2$. Finally, these steps only consider Langmuir-Hinshelwood reactions. In this type of reaction, both
CHAPTER 3. RESULTS: ADSORPTION OF $O_2$ AND CO ON $Au_2^-$

Figure 3.7: Suggested pathway based on thermodynamics (continuous arrows). Competition takes place between desorption and adsorption (dashed and dotted arrows).

reactants coadsorb and then leave the cluster. Another possibility is the Eley-Rideal reaction, where only one of the reactants is adsorbed on the cluster and the other directly reacts with it, without adsorbing.

To illustrate the other possibilities, reaction steps corresponding with desorption are shown as dashed arrows in the reaction path in figure 3.7. However, these limitations do not make our suggestion for a reaction path useless. Kinetic studies require much time and computer power. This reaction path provides a starting point for a kinetic analysis. A full fledged kinetic analysis is beyond the scope of this thesis.

3.6 Accuracy of the data

In order to assess the accuracy of our data, these are compared to reference data from literature and more accurate *ab initio* methods than DFT. There is a well-known error in DFT considering binding to oxygen. Because we are mainly interested in energy differences, 

$$\Delta E_f = E(Au_2O_2^-) - E(Au_2^-) - \frac{\lambda}{2} E(O_2)$$

these errors are partly compensated. To see how much of the overbinding by DFT remains, the binding energies as found in this study are compared to the binding energies as found from various methods by Varganov et al\[26\]. The binding energy of the first and the second oxygen molecule are considered, defined as

$$E_{b1} = E[Au_2^-] + E[O_2] - E[Au_2O_2^-]$$

$$E_{b2} = E[Au_2O_2^-] + E[O_2] - E[Au_2O_4^-]$$
3.6. ACCURACY OF THE DATA

Table 3.4: Differences in energy, free energy at 100 K and free energy at 300 K for the reaction steps in figure 3.7.

<table>
<thead>
<tr>
<th>reaction</th>
<th>$\Delta E$ (eV)</th>
<th>$\Delta G_{100K}$ (eV)</th>
<th>$\Delta G_{300K}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_2^-$ + O$_2$ $\rightarrow$ Au$_2$O$_2^-$</td>
<td>-1.42</td>
<td>-1.16</td>
<td>-0.66</td>
</tr>
<tr>
<td>Au$_2$O$_2^-$ + CO $\rightarrow$ Au$_2$O$_2$CO$^-$</td>
<td>-4.50</td>
<td>-3.58</td>
<td>-3.03</td>
</tr>
<tr>
<td>Au$_2$O$_2$CO$^-$ + CO $\rightarrow$ Au$_2$O$_2$CO$_2$</td>
<td>-1.98</td>
<td>-1.69</td>
<td>-1.23</td>
</tr>
<tr>
<td>Au$_2$O$_2$CO$_2^-$ + O$_2$ $\rightarrow$ Au$_2$O$<em>4$CO$^-$</em>$^2$</td>
<td>-2.04</td>
<td>-1.66</td>
<td>-1.05</td>
</tr>
<tr>
<td>Au$_2$O$<em>4$CO$^-$</em>$^2$ $\rightarrow$ Au$_2$O$_3$CO$^-$ + CO$_2$</td>
<td>+0.82</td>
<td>+0.50</td>
<td>-0.08</td>
</tr>
<tr>
<td>Au$_2$O$_3$CO$^-$ + O$_2$ $\rightarrow$ Au$_2$O$_3$CO$_2$</td>
<td>-2.78</td>
<td>-2.41</td>
<td>-1.89</td>
</tr>
<tr>
<td>Au$_2$O$_3$CO$_2^-$ $\rightarrow$ Au$_2$O$<em>2$CO$^-$</em>$^2$ + CO$_2$</td>
<td>-0.57</td>
<td>-0.85</td>
<td>-1.45</td>
</tr>
</tbody>
</table>

Table 3.5: Binding energies for the first O$_2$ to Au$_2^-$, $E_{b1}$ and the second O$_2$ to Au$_2$O$_2^-$, $E_{b2}$. The CCSD(T) and PW-PW91 data are from Varganov, Olson, Gordon and Metiu[26].

<table>
<thead>
<tr>
<th></th>
<th>CCSD(T)</th>
<th>PW-PW91</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{b1}$</td>
<td>1.07</td>
<td>1.40</td>
<td>1.42</td>
</tr>
<tr>
<td>$E_{b2}$</td>
<td>-0.56</td>
<td>0.71</td>
<td>0.70</td>
</tr>
</tbody>
</table>

where only molecular adsorption is considered.

CCSD(T) is the current ‘gold standard’ in electronic structure calculations. CC is an abbreviation of coupled cluster. This is a method based on Hartree-Fock theory. The name stems from the way the wavefunction is expanded. The letters behind CC tell which excitations are included. In this case, single excitations and double excitations are fully included, and triple excitations within perturbation theory. The more excitations are included, the more accurate the coupled cluster calculation.

The other method, PW-PW91, is a DFT method with different basis set and exchange-correlation functional. These numbers are very close (within 0.2 eV) to our PBE+vdW calculations.

The binding energy of the first oxygen molecule, $E_{b1}$ illustrates the overbinding of DFT. In the binding energy to the second oxygen molecule this is even more pronounced. The negative binding energy indicates that Au$_2$(O$_2$)$_2^-$ is unstable. This is supported by experiments[6]. However, only molecularly bound oxygen is considered. The ground state of Au$_2$O$_4^-$ includes dissociated oxygen. This is 0.7 eV lower in energy than molecularly bound oxygen. That this state is stable is supported by experiments by Kimble et al.[25].

This may be a particularly unfortunate case. Comparison of binding energies of several Au$_2$O$_2$(CO)$_n$ from DFT and CCSD(T) yields an error of 0.45 ± 0.1 eV[8]. Since in our analysis different clusters are compared, only the differences in this error (± 0.1 eV) are not compensated. This will cause the regions on the phase diagrams to appear smaller or larger. Small regions may even disappear. However, the regions with the considered catalyst, Au$_2$O$_2$CO$^-$_$^2$, and reaction intermediate Au$_2$O$_4$CO$^-$_$^2$ extend many orders of magnitude beyond the region of ambient pressures. The energy values considered in the reaction path may change, but in many cases the
gain in energy is very large and likelihood of this reaction occurring based on thermodynamics will hardly change. Some reaction paths will not be favourable anymore, but it is unlikely that this will affect our conclusions.

3.7 Comparison with experiments

The small size of atomic clusters is an advantage for computational simulations, but this size makes experiments difficult and limited experimental results are available. A reason to choose Au\(_2^-\) clusters for this project was the presence of an extensive experimental study by Socaciu et al.\(^\text{[4]}\) with an explanation from theory, allowing for comparison.

Figure 3.8: Experimental setup of Socaciu et al.\(^\text{[4]}\), showing the trajectory of the gold clusters from creation at the sputter targets, through the ion trap where the reaction takes place, to the detector.

The experimental setup is shown in figure 3.8. A sputter target was used to produce the gold clusters, which are then mass selected and thermalized. Next, the clusters enter an ion trap filled with CO and O\(_2\) gas. The pressures of these gases and the temperature are monitored. After a certain reaction time, the contents of the ion trap are analyzed by mass spectrometry. It was found that at 100 K, Au\(_2^-\), Au\(_2\)O\(_2^-\) and Au\(_2\)O\(_2\)CO\(^-\) are present, see figure 3.9. The latter composition is missing at 300 K, where only Au\(_2^-\) and Au\(_2\)O\(_2^-\) were found.

Figure 3.9: This mass spectrometry spectrum from Socaciu et al. shows the species which are found at the detector in figure 3.8.

The authors assumed that Au\(_2\)O\(_2\)CO\(^-\) was the reaction intermediate. Using dft, several structures of this composition were optimized and a reaction path using those was constructed.
They propose that Au$_2^-$ adsorbs first O$_2$ and then CO, forming Au$_2$O$_2$CO$^-$. This reacts with another CO to produce 2 CO$_2$ molecules. This is one of the possible reaction paths shown in figure 3.7. They considered the simplest path, but their kinetic analysis leaves the possibility open of intermediate steps and more complicated pathways. Several of these are proposed in figure 3.7. Our results are thus in satisfactory agreement with the experimental results of Socaciu et al.

### 3.7.1 Equilibrium

Another experimental group, Kimble et al.\[25\], looked at the reaction of CO with oxidized gold clusters. They found Au$_2$O$^-$, Au$_2$O$_2^-$, Au$_2$O$_3^-$ and Au$_2$O$_4^-$ after reaction time, see figure 3.10.

![Figure 3.10: Mass spectrum obtained by Kimble, Moore, Johnson, Castleman Jr, Bürgel Mitric and Bonačić-Koutecký\[25\], showing the species found after an experiment in a fast flow reactor. Dissociated oxygen is found here.](image)

According to our calculations, Au$_2$O$^-$, Au$_2$O$_3^-$ and Au$_2$O$_4^-$ are more thermodynamically favourable than Au$_2$O$_2^-$,. Since Socaciu et al. found only Au$_2$O$_2^-$, also when no CO was present in the ion trap, this raises the question whether this experiment is in equilibrium.

Thermodynamics only considers the equilibrium situation, so if the experiment is not in equilibrium, it is of limited value for comparison.

### 3.8 Comparison with other systems

#### 3.8.1 The size effect: Comparison with Au$^-$

To study the effect of size on the catalysis of the CO oxidation reaction by gold, the phase diagram of Au$^-$ is compared to the phase diagram of Au$_2^-$. The top of the phase diagram looks very similar to that of Au$_2^-$. In both cases, an isomer with both a CO$_2$ and a CO$_3$ group occupies the right upper corner. When less oxygen is present, an isomer with two CO$_2$ groups is dominant. The bottom of the phase diagram, at low CO pressure, the phase diagrams differ more. Where for Au$_2^-$ isomers with only oxygen, Au$_2$O$_3^-$, Au$_2$O$_4^-$ and Au$_2$O$_5^-$ are visible, for Au$^-$ only AuO$_2$ appears. For higher oxygen pressures, AuO$_3$CO$^-$ and AuO$_4$CO$^-$ appear. This can be explained from the electronic structure of gold. Au$^-$ has a closed shell structure, which makes it hard to bind to the strongly electronegative oxygen. This is much easier for Au$_2^-$, which has an open shell structure with one free electron.
Another difference is the binding strength of the different isomers to CO$_2$. Almost all of the isomers of the monomer anion bind tightly to CO$_2$, see table 3.6. Thus, very little changes in the phase diagram upon lowering CO$_2$ pressure from infinity to ambient conditions. The region corresponding to experimental experimental conditions remains. Thermodynamics predicts that equilibrium is reached when all Au$^-$ has been converted into AuO$_3$(CO)$_2^−$. No further reactions would occur and no catalysis of the CO oxidation reaction would take place.

### 3.8.2 The charge effect: Comparison with Au$_2$

Prior to this work, Elizabeth C. Beret has studied Au$_2$ using the same methods. The phase diagrams obtained for Au$_2$ are shown in figure 3.12.

Several similarities between these phase diagrams and those for Au$_2^-$ can be observed. Al-

<table>
<thead>
<tr>
<th>R$^-$CO$_2$</th>
<th>R</th>
<th>$\Delta G_f$ (eV)</th>
<th>$p_{CO_2}^{eq}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuO$_3$(CO)$_2^−$</td>
<td>AuO$_2$CO$^−$</td>
<td>−5.04</td>
<td>2 E−12</td>
</tr>
<tr>
<td>AuO$_2$(CO)$_2^−$</td>
<td>AuOCO$^−$</td>
<td>−4.42</td>
<td>1 E+00</td>
</tr>
<tr>
<td>AuO$_4$(CO)$_2^−$</td>
<td>AuO$_3$CO$^−$</td>
<td>−3.67</td>
<td>7 E+25</td>
</tr>
<tr>
<td>AuO$_4$(CO)$^−$</td>
<td>AuO$_3$$^−$</td>
<td>−3.20</td>
<td>6 E−19</td>
</tr>
<tr>
<td>AuO$_3$(CO)$^−$</td>
<td>AuO$_3$$^−$</td>
<td>−3.20</td>
<td>3 E−07</td>
</tr>
<tr>
<td>AuOCO$^−$</td>
<td>Au$^−$</td>
<td>−2.42</td>
<td>1 E−07</td>
</tr>
<tr>
<td>AuO$_2$(CO)$^−$</td>
<td>AuO$^−$</td>
<td>−2.33</td>
<td>2 E−17</td>
</tr>
<tr>
<td>AuO(CO)$_2$</td>
<td>AuCO$^−$</td>
<td>−2.07</td>
<td>8 E−08</td>
</tr>
</tbody>
</table>

Table 3.6: CO$_2$ equilibrium pressures for AuO$_x$CO$_y$$^−$. The free energies of formation $G_f$ are based on low-pressure conditions, $p_{O_2} = 10^{-6}$atm, $p_{CO} = 10^{-6}$atm, $p_{CO_2} = 10^{-8}$atm.
3.8. COMPARISON WITH OTHER SYSTEMS

(a) $p_{CO_2} = \infty$: Reaction intermediates

(b) $p_{CO_2} = 10^{-3}$ atm: Catalysts

Figure 3.12: Phase diagrams for Au$_2$O$_x$CO$_y$ at 300 K.
though the most stable structures are different due to the different electronic structures, in both cases structures of the form R-CO$_3$ or RCO$_2$ are favoured. CO$_2$ is bound differently to the neutral dimer, with one oxygen bound to a gold atom instead of the carbon as in the negatively charged dimer. Due to the electronegativity of oxygen, more charge can be pulled away and accommodated on the CO$_2$ if this is bound by carbon. This stabilized the negatively charged structures, but not the neutral ones. All isomers where oxygen and carbon monoxide coadsorb desorb CO$_2$ at atmospheric CO$_2$ pressure.

The fact that closed shell systems bind less well to oxygen than systems with a valence electron can also be seen in the phase diagrams of Au$_2$ and Au$_2^-$. In ambient conditions, adsorbing CO on Au$_2$ is preferred to adsorbing O$_2$. The catalyst then, is Au$_2$(CO)$_2$. 
Results: Wet gold clusters

Catalysis by gold particles not only occurs at low temperatures, but also in a moist environment. This makes gold clusters suitable catalysts in ambient conditions. Water is even reported to enhance the rate of the CO oxidation reaction. It is unclear, however, how this can be explained.

Several theories have been suggested in the literature. Most of them suggest an important role for the surface. This has been confirmed by experiments with gold clusters on different supports, where the effect of water on the reaction differed considerably\(^{[27]}\). However, there are indications that catalysis of the CO oxidation reaction with unsupported clusters is also enhanced by water. Many different reaction mechanisms have been proposed, with OH\(^{[28]}\), OOH\(^{[29]}\), CO\(_2\)H\(^{[28]}\) and CO\(_3\)H\(^{[27]}\)\(^{[29]}\) groups as suggested reaction intermediates and a suggested role for water in the activation of oxygen\(^{[27]}\). In this part *ab initio atomistic thermodynamics* is used to see whether this can shed some light on the role played by water.

### 4.1 Water and oxygen

A first step is to see what happens to the binding of oxygen if only water and oxygen are present. The ground state isomers of all configurations can be seen in tables 4.1 and 4.2. From this, it can be concluded that the formation of -OH groups is preferred. OOH groups, another suggested intermediate\(^{[28]}\), are not found among the ground states. For the neutral dimer, isomers of the form R-H\(_2\)O are also observed. In the anions, covalently bound H\(_2\)O groups are not stable. Instead, H\(_2\)O is bound by dipole interaction. This is the preferred state for Au\(_2\)O(H\(_2\)O)\(_n\)\(^−\) and for Au\(_2\)O\(_2\)H\(_3\)\(^−\) and Au\(_2\)O\(_3\)H\(_2\)\(^−\).

Most cases show no major changes in geometries upon the inclusion of hydrogen. It can be seen that the molecular oxygen in Au\(_2\)\(^−\) and Au\(_2\)O\(_2\)H\(^−\) is replaced by dissociated oxygen upon the addition of an H atom, allowing for the formation of OH groups.
### Table 4.1: The ground state isomers of Au$_2$O$_x$H$_w$

<table>
<thead>
<tr>
<th>Au$_2$</th>
<th>O</th>
<th>O$_2$</th>
<th>O$_3$</th>
<th>O$_4$</th>
<th>O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>H</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>H$_2$</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
</tr>
<tr>
<td>H$_3$</td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
<td><img src="image19.png" alt="Image" /></td>
</tr>
<tr>
<td>H$_4$</td>
<td><img src="image20.png" alt="Image" /></td>
<td><img src="image21.png" alt="Image" /></td>
<td><img src="image22.png" alt="Image" /></td>
<td><img src="image23.png" alt="Image" /></td>
<td><img src="image24.png" alt="Image" /></td>
</tr>
</tbody>
</table>

### Table 4.2: The ground state isomers of Au$_2$O$_x$H$_w^-$

<table>
<thead>
<tr>
<th>Au$_2^-$</th>
<th>O</th>
<th>O$_2$</th>
<th>O$_3$</th>
<th>O$_4$</th>
<th>O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td><img src="image25.png" alt="Image" /></td>
<td><img src="image26.png" alt="Image" /></td>
<td><img src="image27.png" alt="Image" /></td>
<td><img src="image28.png" alt="Image" /></td>
</tr>
<tr>
<td>H</td>
<td><img src="image29.png" alt="Image" /></td>
<td><img src="image30.png" alt="Image" /></td>
<td><img src="image31.png" alt="Image" /></td>
<td><img src="image32.png" alt="Image" /></td>
<td><img src="image33.png" alt="Image" /></td>
</tr>
<tr>
<td>H$_2$</td>
<td><img src="image34.png" alt="Image" /></td>
<td><img src="image35.png" alt="Image" /></td>
<td><img src="image36.png" alt="Image" /></td>
<td><img src="image37.png" alt="Image" /></td>
<td><img src="image38.png" alt="Image" /></td>
</tr>
<tr>
<td>H$_3$</td>
<td><img src="image39.png" alt="Image" /></td>
<td><img src="image40.png" alt="Image" /></td>
<td><img src="image41.png" alt="Image" /></td>
<td><img src="image42.png" alt="Image" /></td>
<td><img src="image43.png" alt="Image" /></td>
</tr>
</tbody>
</table>

![Image](image44.png)
4.1.1 Phase diagrams

To see which structures are the most energetically favourable in different conditions, the free energy of formation

\[ \Delta G = G_{\text{Au}_2\text{O}_x\text{H}_w} - \frac{w}{2}\mu_{\text{H}_2\text{O}} - \left( x - \frac{w}{2} \right) \mu_{\text{O}} \]

has been calculated and the results are again visualized in phase diagrams. These diagrams have a horizontal line at \( \mu_{\text{H}_2\text{O}} = 0.91 \text{ eV} \). Below this line, water is gaseous at all temperatures and pressures, given by the experimental critical point of water\[^{[30]}\]. Realistic water pressures at 300 K are generally above this line. Wallace et al.\[^{[31]}\] consider a water pressure of \( 10^{-3} \) at 300 K, corresponding to \( \mu_{\text{H}_2\text{O}} = -0.48 \text{ eV} \), at which water is also gaseous. Therefore, the phase diagrams are extended above the \( \mu_{\text{H}_2\text{O}} = 0.91 \text{ eV} \) line.

![Figure 4.1: Phase diagram for \( \text{AuO}_x\text{H}_w \) clusters at 300 K.](image)

The phase diagrams in figure show that for \( \text{Au} \), \( \text{Au}_2 \) and \( \text{Au}_2^- \) the presence of water changes the phase diagram markedly. In regions with realistic water pressures, the inclusion of one or more bound hydrogens to cluster is preferred for \( \text{Au} \), \( \text{Au}_2 \) and \( \text{Au}_2^- \), see figures 4.1 and 4.1.1. Compared to the neutral dimers, the dimer anions bind easier to oxygen and also to species which include hydrogen.

4.1.2 Comparison with experiment

Experiments studying the effect of water on gold clusters in the gas phase are rare, but there is one experiment on the interaction of \( \text{AuN}^- \) available from Wallace and Whetten\[^{[31]}\]. In their setup charged gold clusters are formed and equilibrated by laser vaporization of a rotating and translating gold rod in a high-pressure helium/\( \text{H}_2\text{O} \) flow stream and exposed to a second gas pulse with helium/O. They found several species of the form \( \text{AuN(OH)}_{0-2}(\text{H}_2\text{O})_{0-2}^- \). Clusters of the form \( \text{AuN(OH)}^- \) were found to be strongly bound.
4.2 CO oxidation

Upon the addition of CO, much more compositions are possible and the phase diagram gets much more complicated. Which isomer is thermodynamically preferred depends on the pressures of O₂, CO, H₂O and CO₂. In principle, also the water gas shift reaction

\[ CO + H₂O \rightarrow H₂ + CO₂ \]

could occur, but this possibility is not taken into account due to its high reaction temperature[27].

The stability of the isomer depends now on four gases, with

\[ \Delta G = G_{Au_2O_xH_w} - x \mu_{H₂O} - y \mu_{CO} \]

being the free energy of formation, which depends on the pressures of H₂O, CO and O₂. As for the reaction without water, CO₂ dissociation needs to be taken into account. This is again done by calculating the pressure \( p_{CO₂} \) where the reaction

\[ R - CO₂ \rightleftharpoons R + CO₂(g) \]

is in equilibrium. Below this pressure CO₂ desorption is more favourable. This has the effect that structures may be the most thermodynamically favourable isomers, but are not stable towards CO₂ dissociation. These are possible reaction intermediates and are visible in a phase diagram where \( p_{CO₂} = \infty \), because at infinite CO₂ pressure desorption of CO₂ is never preferred. At higher pressures, some structures desorb CO₂. Which is the most favourable stable structure thus not only depends on O₂, CO or H₂O pressure, but also on CO₂ pressure. The phase diagrams in figure 4.3 are cross sections at \( \mu_{H₂O} = -0.48 \text{ eV} \), corresponding to \( p_{H₂O} = 10^{-3} \text{ atm} \), at different pressures of CO₂. The structures and equilibrium CO₂ pressures of the compositions that appear in the phase diagrams can be found in table 4.2.

When CO is present, the adsorption of CO is in most circumstances preferred over the adsorption of hydrogen in the case of Au₂⁻. Figure 4.3 shows that in the region of interest,
4.2. CO OXIDATION

Figure 4.3: Phase diagram for Au$_2$O$_x$H$_w$(CO)$_y^-$ clusters at 300 K at $p_{CO_2} = \infty$: reaction intermediates.

Table 4.3: $CO_2$ equilibrium pressures for several isomers.

<table>
<thead>
<tr>
<th>$R-CO_2$</th>
<th>$R$</th>
<th>$p_{CO_2}^{eq}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_2$O$_4$(CO)$_2^-$</td>
<td>Au$_2$O$_2$CO$^-$</td>
<td>3 E$-07$</td>
</tr>
<tr>
<td>Au$_2$O$_2$H(CO)$_2^-$</td>
<td>Au$_2$O$_2$HCO$^-$</td>
<td>1 E$+17$</td>
</tr>
<tr>
<td>Au$_2$O$_2$(CO)$_2^-$</td>
<td>Au$_2$OCO$^-$</td>
<td>3 E$+01$</td>
</tr>
<tr>
<td>Au$_2$O$_2$H(CO)$_2^-$</td>
<td>Au$_2$OHCO$^-$</td>
<td>2 E$+00$</td>
</tr>
<tr>
<td>Au$_2$O$_2$HCO$^-$</td>
<td>Au$_2$OH$^-$</td>
<td>6 E$-05$</td>
</tr>
</tbody>
</table>

Au$_2$O$_4$CO$_2^-$ is still the favoured isomer at high CO$_2$. A small region with Au$_2$O$_2$HCO$_2^-$ is visible when less oxygen is present and Au$_2$O$_2$CO$_2^-$ remains the favoured isomer in a large range of low oxygen conditions. In very low oxygen conditions Au$_2$O$_2$HCO$_2^-$ is the most thermodynamically favourable isomer. More change can be observed in the bottom region of the phase diagram, in the region with low CO. There species with coadsorbed O and H are seen, as expected from figure 4.3. Interesting is the appearance of an isomer with the composition Au$_2$O$_2$HCO$^-$: This is an hydrated carbonate, a suggested reaction intermediate. Its structure is very similar to Au$_2$O$_2$CO$^-$, but for the hydrated carbonate it is much more favourable to dissociate CO$_2$, see table 4.2. The $CO_2$ equilibrium pressure is 6 E$-05$ compared to 3 E$-18$ atm for Au$_2$O$_2$CO$^-$.

The hydrated carbonate is the most thermodynamically favourable stable isomer at $p_{CO_2} = 10^{-3}$ atm, see figure 4.2, when Au$_2$O$_4$CO$_2^-$ is not taken into account. This is done because its formation is questionable, because many ligand adsorptions without desorbing in the mean time are necessary. Also, not showing Au$_2$O$_4$CO$_2^-$ makes the position of Au$_2$O$_2$HCO$^-$ more clear. At lower CO$_2$ pressure Au$_2$O$_2$HCO$^-$ dissociates and it can be seen in figure 4.2 that Au$_2$O$_2$CO$^-$ is the most favourable stable isomer, as in the case without water.

**Au$_2$ in the presence of CO and water**

Phase diagrams when water is present have also been made for neutral Au$_2$, see figure 4.2.
It can be seen in figure 4.2 that the neutral dimer binds less easy to oxygen, and also to hydroxyl groups. Its phase diagram changes less upon the addition of water than the phase diagram of the dimer anion and both predicted catalyst and reaction intermediate do not contain hydrogen. Water is thus expected to have a less important role than for the negatively charged cluster, but it might still have a part in the kinetics of the reaction.

4.3 Influence on pathways

The presence of water greatly increases the number of pathways. As the phase diagrams show, the binding of OH groups is thermodynamically favourable. The experiments of Wallace and Whetten show that this happens in practice.

The gold dimer anion binds hydrogen more easily than the neutral dimer, possibly due to the gain of a singlet spin state. However, the singlet spin state also makes the reaction with oxygen more complicated, because oxygen is a triplet. This would make the reaction product also a triplet, which is rarely the ground state of a certain composition and the adsorption of oxygen thus becomes less energetically favourable.

Creating a reaction path with water is less straightforward than when just taking O$_2$ and CO adsorption into account, because contrary to the case of O$_2$ or CO, adsorption cannot be limited to entire molecules. That way, compositions containing only one H could never be reached. Therefore, the addition of OH is considered as $\frac{1}{2}H_2O + \frac{1}{4}O_2$. An example pathway is shown in table 4.3. This pathway starts from the catalyst at $p_{CO_2} = 10^{-3}$ atm, Au$_2$O$_2$CO$^-$. It also contains the catalyst at $p_{CO_2} = 10^{-7}$ atm, Au$_2$O$_2$HCO$^-$. The pathway continues to the reaction intermediates Au$_2$O$_2$H(CO)$_2$ and Au$_2$O$_3$HCO$^-$. Although Au$_2$O$_4$CO$^-$ is the most thermodynamically favourable reaction intermediate, its formation requires several adsorption steps without desorbing CO$_2$ or adsorbing OH in between. Since this might be difficult, this isomer is not included.

This pathway is largely downhill. The energies given in table 4.3 are energies at 0 K. When
### 4.3. INFLUENCE ON PATHWAYS

Table 4.4: Structures of the isomers that appear in the phase diagrams and the pressure below which desorption is more favourable.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>$p_{\text{CO}_2}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_2$O$_4$(CO)$_2^-$</td>
<td><img src="image1" alt="Structure" /></td>
<td>$3 \times 10^{-7}$</td>
</tr>
<tr>
<td>Au$_2$O$_3$H(CO)$_2^-$</td>
<td><img src="image2" alt="Structure" /></td>
<td>$1 \times 10^{17}$</td>
</tr>
<tr>
<td>Au$_2$O$_2$(CO)$_2^-$</td>
<td><img src="image3" alt="Structure" /></td>
<td>$3 \times 10^{01}$</td>
</tr>
<tr>
<td>Au$_2$O$_2$H(CO)$_2^-$</td>
<td><img src="image4" alt="Structure" /></td>
<td>$2 \times 10^{00}$</td>
</tr>
<tr>
<td>Au$_2$O$_2$HCO$^-$</td>
<td><img src="image5" alt="Structure" /></td>
<td>$6 \times 10^{-5}$</td>
</tr>
<tr>
<td>Au$_2$O$_3$H$_2^-$</td>
<td><img src="image6" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>Au$_2$O$_2$H$_3^-$</td>
<td><img src="image7" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>Au$_2$O$_3$HCO$^-$</td>
<td><img src="image8" alt="Structure" /></td>
<td>$3 \times 10^{-07}$</td>
</tr>
<tr>
<td>Au$_2$(CO)$_4^-$</td>
<td><img src="image9" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>Au$_2$O$_2$CO$^-$</td>
<td><img src="image10" alt="Structure" /></td>
<td>$3 \times 10^{-18}$</td>
</tr>
</tbody>
</table>
CHAPTER 4. RESULTS: WET GOLD CLUSTERS

(a) Reaction intermediates: \( p_{\text{CO}_2} = \infty \)

(b) Catalysts: \( p_{\text{CO}_2} = 10^{-3} \text{atm} \)

Figure 4.5: Phase diagram \( \text{Au}_2\text{O}_x\text{H}_n\text{CO}_y \) clusters at 300 K at \( p_{\text{H}_2\text{O}} = 10^{-3} \text{atm} \).

<table>
<thead>
<tr>
<th>reaction</th>
<th>( \Delta E ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Au}_2\text{O}_2\text{CO}^- + \text{CO} \rightarrow \text{Au}_2\text{O}_2\text{CO}_2^- )</td>
<td>-1.98</td>
</tr>
<tr>
<td>( \text{Au}_2\text{O}_2\text{CO}_2^- \rightarrow \text{Au}_2\text{OCO}^- + \text{CO}_2 )</td>
<td>+0.29</td>
</tr>
<tr>
<td>( \text{Au}_2\text{OCO}^- + \text{OH} \rightarrow \text{Au}_2\text{O}_2\text{HCO}^- )</td>
<td>-0.22</td>
</tr>
<tr>
<td>( \text{Au}_2\text{O}_2\text{HCO}^- + \text{CO} \rightarrow \text{Au}_2\text{O}_2\text{H}(\text{CO})_2^- )</td>
<td>-0.48</td>
</tr>
<tr>
<td>( \text{Au}_2\text{O}_2\text{H}(\text{CO})_2^- \rightarrow \text{Au}_2\text{OHCO}^- + \text{CO}_2 )</td>
<td>-0.43</td>
</tr>
<tr>
<td>( \text{Au}_2\text{OHCO}^- + \text{O}_2 \rightarrow \text{Au}_2\text{O}_2\text{HCO}^- )</td>
<td>-1.32</td>
</tr>
<tr>
<td>( \text{Au}_2\text{O}_3\text{HCO}^- \rightarrow \text{Au}_2\text{O}_2\text{CO}^- + \text{OH} )</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Table 4.5: A reaction circle with water, with differences in energy at 0 K.

considering free energies at 300 K, the desorption of \( \text{CO}_2 \) in from \( \text{Au}_2\text{O}_2\text{CO}_2^- \) in the second step also becomes energetically favourable.

Wetting of clusters

Thus far, only covalent absorption of -OH groups is considered. However, even if water does not bind covalently to gold clusters, it might still have a role in the reaction. Water molecules are attracted to the gold cluster anions due to the dipole interaction and surround it, as demonstrated by the molecular dynamics simulations. This is called wetting. This phenomenon has been observed experimentally by Beyer et al.\cite{32}. In this experiment, clusters of the form \( \text{Au}_2(\text{H}_2\text{O})_N^- \) with \( N \) up to 10 were found creation of the gold clusters by laser vaporization. In high vacuum, only clusters with \( N = 1 \) and \( N = 2 \) remain.

The role of wetting on the CO oxidation reaction is unclear. Another experiment by Wallace and Whetten\cite{33} has been done to study the effect of water on the binding of CO to gold. The same setup as in their experiment with water and oxygen (see section 4.1.2) has been used and this time CO and H\(_2\)O instead of O\(_2\) and H\(_2\)O are the reacting gases. They reported that H\(_2\)O
4.4 MOLECULAR DYNAMICS

aided in CO adsorption. When only H$_2$O was present at 300 K, Au$_2^-$ and Au$_2$H$_2$O were found. When CO was also present, Au$_2^-$ and Au$_2$CO$^-$ were the only found species. The latter is not found under dry conditions. Wallace et al. propose a switching reaction where H$_2$O on the cluster was replaced CO. This agrees well with the found dipole binding, where H$_2$O pulls away charge from the cluster, thus making binding with CO easier. At lower temperatures bigger compositions were found, corresponding to Au$_2$(H$_2$O)$_L$(CO)$_M^-$. Unfortunately, this experiment was not repeated with O$_2$, CO and H$_2$O present. It would be interesting to compare the species found there with our phase diagrams.

4.4 Molecular Dynamics

To further analyze the interaction between gold dimer anions and water, several molecular dynamics simulations have been performed. Simulations were done with a gold dimer, surrounded by $N$ water molecules with $N \in [1, 6]$. In all simulations, H$_2$O has been replaced with D$_2$O. This has the same electronic structure as water, but is heavier. This dampens the vibrations and makes the time integration in molecular dynamics more accurate.

4.4.1 Performance of the thermostat

The simulations were done using the Bussi-Donadio-Parrinello thermostat. To check the performance of this thermostat for the chosen system, the conserved Hamiltonian was monitored, see figure 4.6.

![Figure 4.6: Conserved Bussi-Donadio-Parrinello energy (eV) plotted against time for several timesteps.](figure)

It is clear that the thermostat performs properly for all displayed timesteps. The drifts and oscillations are not too big and there is not much difference between the different timesteps. Bigger timesteps show drifts. Therefore, a timestep of 1 fs will be used for the MD simulations.
CHAPTER 4. RESULTS: WET GOLD CLUSTERS

4.4.2 Radial distribution function

From the visualization of the simulations it is clear that the water molecules stay close to the gold dimer anion. No reactions occur, the water molecules do not bind covalently to water and do not form -OH groups. In a simulation of one oxygen molecule three water molecules and a negative gold dimer anion, Au$_2$O$_2^-$ is formed and the water molecules remain attracted to this cluster by dipole interaction. To quantify the behaviour of the water molecules, the radial distribution function has been made. This function gives the chance of finding a water molecule at a certain distance from the gold dimer. Since the gold dimer is not spherically symmetric but cylindrical, the radial distribution function $g$ is given as a function of two coordinates:

$$g(x + \frac{1}{2} \delta x, y + \frac{1}{2} \delta y) = \frac{n(i)}{\pi [(x + \delta x)^2 - x^2] \delta y}$$

where $n(i)$ is the number of distances within the interval between $x + \delta x$ and $y + \delta y$, divided by the number of water molecules and the number of simulations about which is averaged.

A radial distribution function of the distance between the center of mass of the gold dimer anion and the center of mass of a water molecule is plotted in figure 4.7. This simulation consisted of a gold dimer anion and three water molecules, 20000 iterations with a timestep of 1 fs, for a total simulation time of 20 ps.

![Figure 4.7: Contour plot of the radial distribution function of the distance between the center of mass of gold and the center of mass of a water molecule, from a simulation with three water molecules. The z-axis is in line with the axis between the gold atoms and the origin corresponds to the center of mass of the gold dimer anion.](image)

It can be seen in figure 4.7 that in this simulation the water molecules prefer to be located in line with the gold atom, as shown by the peaks around the z-axis. Another preferred position is in the plane between the gold atoms, at a distance of 3 Å from the axis. For more information about the behaviour of water molecules around the gold dimer anion, the radial distribution functions for simulations with different numbers of water molecules would have to be compared.
Conclusion

The catalysis of the CO oxidation reaction by Au\textsuperscript{2−} has been studied using methods from first principles. Extensive sampling of isomers of the compositions Au\textsubscript{2}O\textsubscript{x}(CO)\textsubscript{y}− has been performed with basin hopping. Several structures not found in literature have been identified. Which composition is the most energetically favourable has been analyzed with ab initio atomistic thermodynamics. This depends on temperature and pressures of oxygen and carbon monoxide and can be displayed in phase diagrams. Many of these structures are able to desorb CO\textsubscript{2}. These are possible reaction intermediates. A second phase diagram has been made with the most energetically favourable structures which are stable towards CO\textsubscript{2} desorption at p\textsubscript{CO\textsubscript{2}} = 10^{-8} atm. At ambient conditions, this is a carbonate structure with the composition Au\textsubscript{2}O\textsubscript{2}CO−. This is our proposed catalyst.

Phase diagrams at 100 K and 600 K have been made to study the effect of temperature. This is important because after adsorption the clusters are hotter than their environment. At higher temperatures adsorption is less favourable.

Using thermodynamics, several reaction paths have been proposed connecting the catalyst and reaction intermediate. These are obtained fully ab initio. Our reaction paths are consistent with experimental results from Socaciu et al.\textsuperscript{[4]}. The pathways and structures found form a starting point for a kinetic study.

Water has been reported to enhance the CO oxidation reaction. The behaviour of clusters towards water has been studied with ab initio atomistic thermodynamics and molecular dynamics. It has been found that hydrated groups are more energetically favourable when only water and oxygen are present. Interestingly, water also binds to gold anions by dipole attraction. This wetting of the clusters might also affect the reaction. When CO is present, clusters where O and CO coadsorb without hydrogen remain dominant. However, a species of the composition Au\textsubscript{2}O\textsubscript{2}HCO−, a hydrated carbonate, has been found to be energetically favourable under certain conditions. This cluster desorbs CO\textsubscript{2} much easier than the carbonate Au\textsubscript{2}O\textsubscript{2}CO−, our suggested catalyst, and might therefore play a role in the reaction. These findings motivate further study.
Bibliography


