Valence Band Properties of the Ruthenium Complex Catalyst Using Ab Initio Theory

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Abstract

Ruthenium complexes has been geometrically optimized with different combinations of basis sets. Using single point calculation, the Density of States and partial Density of States has been calculated. RuIII-OH$_2$ experienced a shift towards higher binding energies. The Ru atom plays a vast role in the contribution to the HOMO level of each complex, dominating in RuII-OH$_2$. The nitrogen atom gives a small contribution for each complex in the HOMO region except for RuII-OH$_2$ where it only appears at higher binding energies. The energy difference between RuII-OH$_2$ and RuIII-OH/RuIV-O is about 1.1 eV whereas it experimentally is shown to be around 1.5 eV for the same complexes.

Introduction

The projection of further increasing consumption in combination with the cumulative nature of CO_2 emissions require invention and development of carbon-neutral energy [1]. With rapid progress in the development in artificial photosynthesis researchers are optimistic of a future alternative energy resource of this kind. In an ideal system CO_2, H_2O and light are combined and result in green energy as it copies the process of natural photosynthesis. Organometallic systems such as the ruthenium complexes discussed in this project are well-known as efficient catalysts for this kind of reactions. In this project the electronic structure of the valence part in the Ru-complexes has been calculated by means of Density Functional Theory (DFT). Basis sets of different kinds has been taken into account for optimizing the structures in order to be fully confident of the stability of the calculations.

This report will try to answer the following questions regarding the Ru-complexes. Are there any clear differences in the electronic structures in the valence band of the complexes? How much does the contribution of the Ru-atom have to the Highest Occupied Molecular Orbital (HOMO) states? Are there other notable contributions to the HOMO region from the other elements? Could these contributions be a part of the explanation of experimental results obtained from these systems?

The experiment and oxidation cycle

By investigating the nature of artificial photosynthesis, as mentioned in the introduction, a number of different Ruthenium complexes can be produced in the process, see Figure 1. These molecules contain a Ru-atom at its centre, two bipyridines, a pyridine and an attached oxide group, an example of the complex $[Ru^{III}(py)(bpy)(OH_2)]^{3+}$ (abbreviated as [RuIII-OH]3+) can be seen in Figure 2.
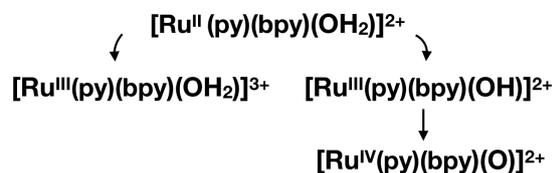

Figure 1: Paths of oxidation processes for the different Ru-complexes of interest.

Solvated complexes have previously been involved in spectroscopy measurements by means of X-ray Photoelectron Spectroscopy (XPS). The information provided of the sample is however insufficient to determine the type of solvated complex. The idea is therefore to identify the valence band structure in order to get a fingerprint of each complex which thereafter, hopefully, can be used for determination in XPS measurements. The valence band simulation can be done by using Density Functional Theory (DFT) as is described in the following Theory section.
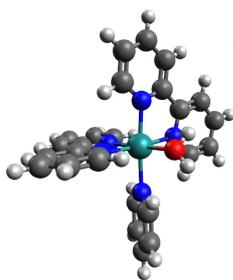
Figure 2: Schematic image of [RuIII-OH]3+

Theory

DFT has been used to calculate the properties of the Ru-complexes. The theory is based on solving the Schrödinger Equation (SE), eq. 1 in order to find all the information needed to describe the system of interest.

$$\hat{\mathcal{H}}\psi = E\psi \tag{1}$$

This well-know equation consists of the Hamiltonian, $\hat{\mathcal{H}}$, which includes the sum of electronic and nuclear kinetic energies, electron-electron, electron-nucleus and nucleus-nucleus potential energies and the total wave-function (wf) of the system, ψ. To save computational time, the wf in DFT is based on the electron density rather than the position in three dimensions as originally proposed by Hohenberg and Kohn. To properly solve the SE for the system, defining the wf is of key interest. This implies choosing a method, often one based on earlier experiences, and a set of basis sets which serves as a description of the atomic orbitals, also called basis functions. The method and basis sets used in this project is described within the section Computational Details. For smaller systems it has been shown that the atomic orbitals can be well-described using Gaussian-type orbitals (GTOs).[2] For big systems such as crystals, one typically uses plane waves instead of local functions. Minimal basis sets contain a minimum set of basis functions to describe all of the electrons on each atom, and can range from a single basis function to hundreds. For larger atoms, basis functions of p-type are added to the basis functions describing the 1s and 2s orbitals. Polarization functions are added due to

a change from symmetry to antisymmetry of the s-orbitals in the case of atomic bonding, when the electronic structure is reorganized. By using linear combinations of the obtained atomic orbitals these are to form a set of molecular orbitals, the result can be seen in Figure 3 and 4 as Density of States.

Computational Details

Geometry Optimization

Geometry optimization of the complexes has been done using the Gaussian 09 program[3]. The program handles Gaussian shaped functions in order to describe the atomic orbitals. Each Ru complex is described by the hybrid functional B3LYP[4, 5, 6, 7], a standard and stable functional for these types of molecules. Multiple basis set combinations have been tested on the complexes to ensure the stability of the calculations. SDD[8] and LANL2DZ[9, 10, 11, 12] was used for Ru. 6-31G(d,p) and 6-311G(d,p), split and triple split valence band basis set with polarization and diffusion, was used for carbon, oxygen, nitrogen and hydrogen atoms.

Results

As a first step, different basis sets were considered for optimization as described in the previous section. These were tested on all complexes but for simplicity, only the calculations made for RuIII-OH will be presented in this report. Eigenvalues are presented as bars as can be seen in the Density of States (DOS) in figure 3 and a convolution with Gaussian curves was added with a full width at half maximum of 0.4 for every complex. As can be seen in Figure 3, the over all shape for the different combinations appear to be similar, both in energy range as in the relative height of the different peaks. The HOMO level appears to lie within the same energy range, with a small shift towards higher binding energies for the combination of 6-311G(d,p) and LANL2DZ.
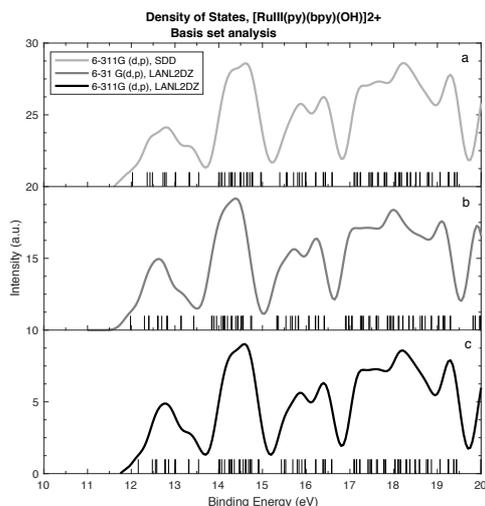
Figure 3: DFT calulations of the total DOS for RuIII-OH with basis SDD or LANL2DZ for Ru and 6-311G(d,p) or 6-31G(d,p) for C, O, N and H.

For a better understanding of the valence band and pinpoint the contribution of the origin of the eigenstates, Partial DOS (pDOS) was calculated with the sets of 6-311G(d,p) and SDD. The plots are mutually shifted by 4.6 eV with respect to RuII-OH$_2$ to match the experimental values, see Figure 4. One can see a shift of about 4 eV towards higher binding energies for the HOMO level of RuIII-OH$_2$ in comparison with HOMO of the other complexes. This might be due to the change in charge of the system, resulting in valence electrons to be more strongly bounded. The different contributions of the element shows that there is an over all contribution of the C, especially in the HOMO range. Nitrogen shows its presence in the HOMO region for all complexes except for RuII-OH$_2$. Comparing the simulated data in Figure 4 with experimental values in Figure 5 was proven to be difficult as the experiment could not validate the presence of the type of complex in the sample as well as the short energy range in which the measurement was done. Despite that, the HOMO level energy difference of RuII-OH$_2$ and the possible mix of RuIII and RuIV complexes in Figure 5 could be noted to be around 1.5 eV. When observing the calculated data in Figure 4 and

comparing the HOMO level in Figure 4a with 4c and 4d, an approximate energy difference of 1.1 eV, similar to the experimental value. The big shift of RuIII-OH$_2$ in the calculated DOS, as mentioned, indicates thus that the mix of RuIII and RuIV in the experimental plot does not include a contribution of RuIII-OH$_2$ complex in the HOMO region.
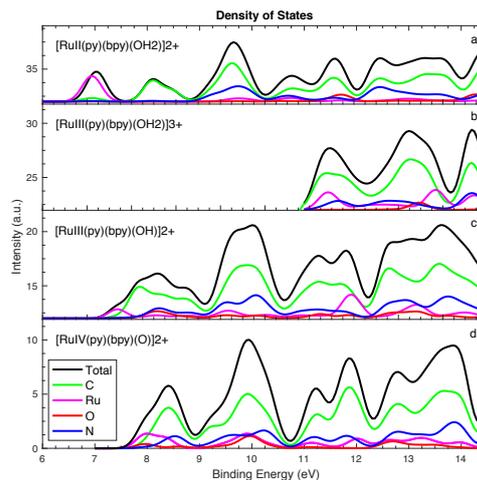

Figure 4: DFT calculations of the total and partial DOS for the different Ru complexes with basis set SDD and 6-311G(d,p) respectively.
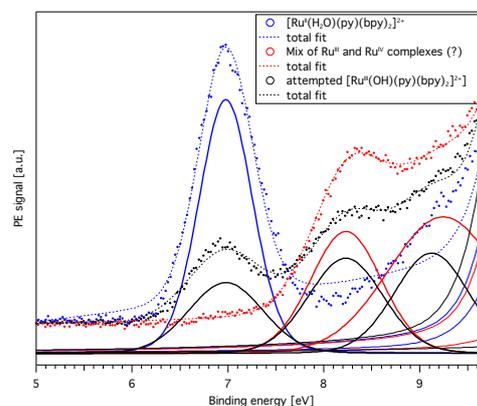

Figure 5: Valence band spectroscopy of solvated Ru-complexes, obtained with XPS from the group of Olle Björneholm at Uppsala University.

Further analysis of the valence orbitals has been

performed with the Molden programme. [13]
The results of this can be seen in Figure 6 which
gives a more clear view of the electronic structure in space. RuII-OH$_2$ shows an evident contribution to the HOMO-level from the Ru-atom
which can also be noticed in Figure 4. This
is interesting as it gives a clear source for the
valence band fingerprint for this particular complex. Figure 6c and 6d shows a contribution
from both the Ru-atom and the attached oxide
group.

Conclusions

We have studied by DFT the valence band
of Ru complexes and thus increasing our understanding of its role in artificial photosynthesis.
The combinations with basis sets of 6-311G(d,p),
6-31G(d,p), SDD and LANL2DZ gave similar
results. Partial DOS was calculated for RuII-OH$_2$, RuIII-OH$_2$, RuIII-OH and RuIV-O and
showed a variation in the HOMO region.

A large shift in the valence band towards
higher binding energies could be noted for the
RuIII-OH$_2$ complex and a difference of about
1.1 eV could be seen between the first peak
in RuII-OH$_2$ and RuIII-OH/RuIV-O, close to
the experimental value of 1.5 eV for the same
molecules. The big shift of RuIII-OH$_2$ is probably due to the higher charge of the complex and
thus pushes the valence band towards higher
energies. By taking this into account, one can
also state the lack of visibility of the RuIII-OH$_2$
complex in the HOMO region of the mixture
of RuIII and RuIV in Figure 5. Ruthenium
appears to be the main source to the valence
band in RuII-OH$_2$ when observing Figure 4a
and this can clearly be seen in the visualized
HOMO in Figure 6a. To summarize this report, the valence band is indeed different for the
investigated molecules. Ruthenium is dominating the valence region for RuII-OH$_2$ and plays
a smaller role in the valence part of RuIII-OH
and RuIV-O. Future work of solvated complexes
might bring a more accurate prediction of the
valence band properties as the experimental
values defines Ru-complexes surrounded by water, whereas this report represents a theoretical
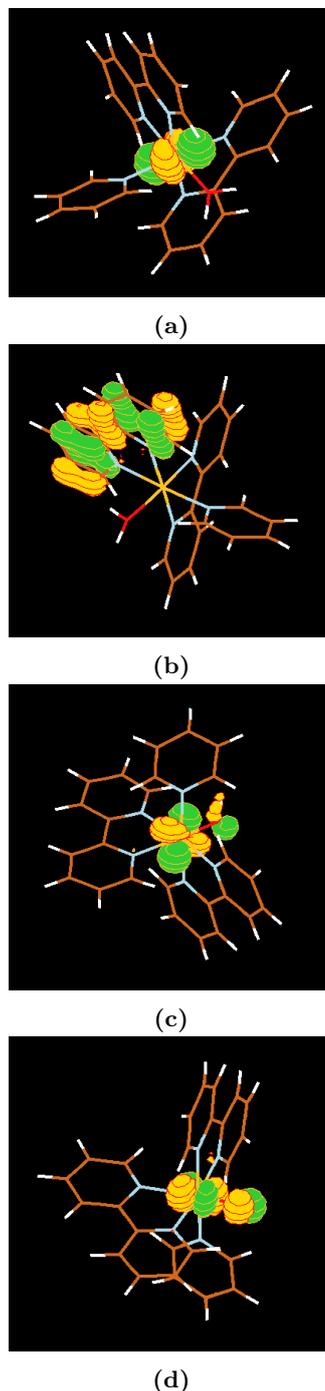framework of a complex in the gas phase.

(a)

(b)

(c)

(d)

Figure 6: HOMO of a) RuII-OH$_2$, b) RuIII-OH$_2$, c) RuIII-OH, d) RuIV-O.

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