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1 Introduction

Today, solar cell technology is an attractive alternative for electrical energy production. The dominating type of solar cells on the market is the silicon solar cell. It is effective and stable, but the production cost is rather high. A different type of solar cell, that is cheaper to produce, is the dye-sensitized solar cell. In contrast to traditional silicon cells, the light absorption and conduction of electrons are here separated. The cell consists in principle of a semiconductor and an electrolyte and, at the interface between these components, a dye. [1]

For further optimization of the dye-sensitized solar cell, an understanding of the molecular structure and processes in the materials included is important. Theoretical methods, like molecular dynamics simulations and quantum chemical calculations are, combined with experiments, powerful tools for describing structure and dynamics at a molecular level, as well as the electronic structure.

1.1 Aim of thesis

The aim of this thesis is to improve the understanding of the electron transfer processes at the dye-electrolyte interface and in the electrolyte in the sun-sensitized solar cell by theoretical calculations. As a model, the interaction between the tris(bipyridine)ruthenium(II) complex and iodide in water is studied. The electronic structure of iodide and triiodide is calculated and compared with experimental spectra.

2 Background

In this section, the components and function of a dye-sensitized solar cell are explained. The dye molecule and the electrolyte are described in more detail, as well as the electron transfer process between them.

2.1 Dye-sensitized solar cells

The dye-sensitized solar cell – also known as a Grätzel cell – is a photoelectrochemical system with three primary components: a semiconductor oxide film, a thin layer of dye molecules and a hole conductor containing a redox couple. The most commonly used semiconductor is TiO$_2$. The dye molecules are attached to the oxide surface at the interface between the semiconductor and the hole conductor. The hole conductor is often an electrolyte based on the iodide/triiodide redox couple. The semiconductor is transparent to visible light, but a photon entering the cell with the right energy will be absorbed by the dye, thereby creating an excited state from which an electron can be injected into the conduction band of the semiconductor. The electron then diffuses through the semiconductor to an external circuit. The hole conductor donates an electron to the oxidized dye, which is ready for another photocycle. The now oxidized hole conductor is in turn reduced by electrons passed through the external circuit. [1] The operation is schematically presented in Fig. 1.

The maximum generated voltage corresponds to the difference between the Fermi level of the electron in the semiconductor and the redox potential of the electrolyte. The most important process is the charge separation of the photoexcited electron–hole pair. In order for the electron to reach the conducting medium without recombining with the hole in the oxidized dye, the hole conductor has to regenerate the dye faster than the time for the back-reaction of the electrons.
Figure 1: The processes in a dye-sensitized solar cell. The most important energy levels are shown: the conduction band of the semiconductor, the highest occupied and lowest unoccupied levels of the dye and the oxidation redox potential of the hole conductor. The arrows show the electronic movement.

with the oxidized dye to take place. The first process typically occurs on a time scale of $10^{-8}$ s, whereas the time for the unwanted back-reaction to take place is in the order of $10^{-6}$ s. Another source of electron loss is if the electron is taken up by an electron acceptor in the electrolyte on its way through the semiconductor. [2, 3] The charge separation takes place at the interface and the transfer rates are to large extent depending on how well the energy levels of the different materials match at the interface, and also of their geometrical structure. [4]

### 2.1.1 The dye molecule

An effective solar cell should absorb as much sunlight as possible and convert it to electrical energy. In order for the electrolyte to give electrons rapidly to the oxidized dye, the redox potential should be sufficiently high. Also, as seen from Fig. 1, the LUMO of the dye should be close to the conduction band of the semiconductor.

The most widely used dyes in the dye-sensitized solar cells are ruthenium-polypyridine complexes. The complexes have anchoring groups that attach to the titanium dioxide surface. [3, 5, 6]

The prototype for the complexes in the Ru(II) polypyridine family is the tris(bipyridine)ruthenium(II) complex ($[\text{Ru(bpy)}_3]^{2+}$). It is a chiral octahedral complex with $D_3$ symmetry (Fig. 2). In the ground state, the ion is a singlet. The Ru(II)/Ru(III) potential is about $+1.25$ V with respect to NHE. [7]

In a recent density functional molecular dynamics study of $[\text{Ru(bpy)}_3]^{2+}$ solvated in water, the distance to the solvent molecules closest to the central atom is calculated to 5-6 Å. The coordination number is shown to be between 5 and 7. [8]
2.1.2 The electrolyte

A hole-conducting medium should regenerate the oxidized dye rapidly, while the process for recombination of electrons traveling through the semiconductor and electron acceptors in the electrolyte should be slow. These characteristics are well met by the most commonly used hole conductor: the iodide/triiodide redox couple, dissolved in an organic solvent.

The regeneration of the dye can be expressed as

\[
dye^+ + 2I^- \rightarrow \text{dye} + I_2^- \tag{1}
\]
\[
2I_2^- \rightarrow I_3^- + I^- \tag{2}
\]

[2]

3 Techniques

The theoretical part of this work consisted of molecular dynamics simulations and quantum chemical calculations. Experimentally, the electronic structure was studied with photoelectron spectroscopy. The general principles of the methods used are described below. For a detailed description of the calculations, see Sections 4 and 5.

3.1 Molecular dynamics

In molecular dynamics (MD), the force on the individual particles of a system is calculated. The particles are allowed to move under the constant force from its neighbors for a short timestep. The forces for the new positions are thereafter calculated. By numerical integration of Newton’s equations of motion for \( N \) particles

\[
\overrightarrow{F_i} = m \frac{d}{dt} \overrightarrow{x_i} = m \overrightarrow{a_i}, \quad i = 1, 2, 3, \ldots, N, \tag{3}
\]
information about how all the particles in the system move over a period of time can be obtained. This requires that an appropriate interatomic potential is specified, as well as well-chosen initial and boundary conditions [9, 10].

3.1.1 Setting up a simulation

The force field can be separated into a term for the interactions within the molecule (bonded interactions) and a term for the intermolecular (nonbonded) interactions:

\[ U = U_{\text{bonded}} + U_{\text{nonbonded}} \]  

Often, it is assumed that the potential can be described as a sum of pairwise interactions between the particles, which reduces the computational cost much.

An ensemble for the simulation has to be chosen. Within this ensemble, certain thermodynamic quantities, like pressure, volume, temperature or number of particles, are fixed in the simulation cell.

The computational cost of an MD simulation grows rapidly with the number of particles and a real bulk system is in practice impossible to simulate. Instead, periodic boundary conditions (PBC) can be used. The simulation cell, containing a relatively small number of particles, is then replicated in all directions. A particle exiting the cell will reappear at the position corresponding to where it entered the nearest image. The particles will hence experience the same forces as in bulk fluid. [11, 10]

3.1.2 Trajectory analysis

With MD, information about the thermodynamics, structure and dynamics of a system can be obtained. Examples of thermodynamic properties are the energy, heat capacity and pressure. Dynamic information available is e.g. diffusion coefficients. [10]

The structure of the system can be described with radial distribution functions (RDF). The RDF gives the probability of finding two particles separated by the distance \( r \), relative to a uniform distribution. A spatial distribution function (SDF) gives the three-dimensional distribution of particles in a coordinate system. [10, 12]

3.2 Quantum chemistry

The foundation of quantum chemistry is the quantum mechanical principles. Any molecular system, i.e. electrons moving in a nuclear potential, can be described by a wavefunction \( \Psi \) that depends on the nuclear and electronic positions. The wavefunction is given as a solution of the Schrödinger equation

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

where the Hamilton operator \( \hat{H} \) contains the potential energy due to the electrostatic interaction between nuclei and electrons in the system and the nuclear and electronic kinetic energies.

According to theory, every property of a system can be obtained with quantum mechanics. In practice, however, the Schrödinger equation can only be solved exactly for one-electron systems – in all other cases approximations have to be made. In the Born-Oppenheimer approximation it is assumed that the nuclear and electronic motions – due to the much smaller mass of the electrons – can be separated. The total wave function can then be written as a product of an electronic and a nuclear wave function. In the electronic Schrödinger equation, the positions of
the nuclei are parameters only. Hence, the electronic energy eigenvalues can be obtained as a function of the nuclear position. [10, 13]

3.2.1  Ab initio methods

In ab initio ("from the beginning") methods, no empirical data are used, but the models are purely mathematical. The standard type of ab initio calculations is the Hartree-Fock (HF) method, where the electrons are assumed to move in the average potential created by all the other electrons. The wave function of an N-electron system is approximated with a single Slater determinant, which is an antisymmetric product of the N spin orbitals. This form of the wave function assures that the Pauli principle is satisfied.

The Hartree-Fock energy is found by optimizing the spin orbitals \( \chi_i \) in the Slater determinant in order to give the lowest energy. As a starting point, trial orbitals are used. The Hartree-Fock equations

\[
\hat{F} \chi_i = \epsilon_i \chi_i, \tag{6}
\]

where \( \hat{F} \) is the Fock operator and \( \epsilon_i \) the energy eigenvalue for orbital \( \chi_i \), are then solved iteratively. The Fock operator contains three terms: the core Hamiltonian for the kinetic energy of one electron and its electrostatic attraction to the nuclei, the Coulomb operator describing the repulsion from all other electrons on one electron and - as a consequence of the antisymmetry of the electronic wave function - the exchange operator. [14, 10]

The Hartree-Fock method does not take the fact that electrons with opposite spins "avoid" each other at small distances - electron correlation - into account. The electron-electron repulsion will therefore be overestimated. The correlation energy is defined as the difference between the Hartree-Fock and the exact energy. Other techniques, like configuration interaction (CI), multi-configuration self-consistent field (MCSCF), Møller-Plessett perturbation theory (MPn), and coupled cluster (CC) account for the correlated motion of the electrons. The exact energy is obtained for a full CI in the limit of an infinite basis set. [10]

An important approach within MCSCF is the Complete Active Space (CAS) SCF method, where the occupied molecular orbitals are separated into inactive and active orbitals. The inactive orbitals are all doubly occupied. For the active orbitals (CAS), the number of electrons and total spin is given and all possible electronic configurations are then included in the wave function.

In the Restricted Active Space (RAS) SCF method, the active orbitals are divided into three subspaces: one where a maximum number of holes is allowed, one where all possible configurations are allowed, and one where a maximum number of electrons is allowed.

The energy obtained with MCSCF can be improved by adding a correction to the multireference wave function. This method is called multireference perturbation theory. With CASPT\( n \), a perturbation of the \( n \):th order is added to CASSCF wave function. [15, 10]

3.2.2 Density functional theory

Density functional theory (DFT) uses functionals of the electron density for determination of the electronic properties. It is today one of the most commonly used techniques, due to its high accuracy at relatively low computational cost. The contributions to the total energy can all be written as functionals of the charge density \( \rho \), which is a function of the electronic position \( \mathbf{r} \) only. The total energy within Kohn-Sham DFT, where non-interacting electrons are assumed to move in an effective potential, can be expressed as

\[
E = E_k[\rho(\mathbf{r})] + E_N[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})], \tag{7}
\]
where $E_k[\rho]$ represents kinetic energy of a system of non-interacting electrons (with the same density as the real system), $E_{Ne}[\rho]$ and $E_H[\rho]$ the Coulombic nucleus-electron attraction and Hartree electron-electron repulsion, respectively, and $E_{XC}[\rho]$ is the electron-electron exchange-correlation energy.

The only term that cannot be determined well with ab initio methods is the exchange-correlation term. There are three main classes of approximations for treating this term:

1. The local density approximation (LDA) treats the density as a uniform electron gas.
2. General gradient approximations (GGA) take into account the non-uniformity of the electron density.
3. Hybrid functionals combine HF and DFT approximations to the exchange energy together with a functional for electron correlation.

3.2.3 Basis sets

In quantum chemical calculations, the basis sets are typically linear combinations of atomic Gaussian functions\(^1\), centered on atoms. In a minimal basis set, only the minimum number of basis functions needed to describe the orbitals on each atom is used. For a better description, the number of basis functions in a minimal basis can be multiplied and a double, triple, etc. \(\zeta\) basis set is then obtained. Another approach is to increase the number of basis functions describing the valence orbitals and let fewer basis functions represent the inner shells. This is called a split-valence basis set.

If a finite set of basis functions is used, the basis functions of two molecules approaching each other will overlap. The electronic structure of each molecule will then be better described than at larger separation distances. This will lead to an error in interaction energies – calculated as the difference between the energy of the interacting molecules and of the molecules at infinite distance from each other – called basis set superposition error (BSSE). A way of estimating this discrepancy is by counterpoise correction. In the calculation of the energy of the individual molecules, ‘ghost functions’ of the other molecule are then placed nearby. No nuclei or electrons of the other molecule are included in the calculation, however. [10]

3.2.4 The polarizable continuum model

A method for modeling solvation effects is the polarizable continuum model (PCM). The computer cost for treating the individual solvent molecules quantum mechanically would be tremendous. With PCM, the solvent is instead described as a polarizable continuum and the van der Waals spheres of the atoms in the solute define a cavity in the solvent. The molecular free energy is then computed as the sum of the electrostatic, the dispersion-repulsion and the cavitation energies. [17]

3.3 Photoelectron spectroscopy

The basis for the photoelectron spectroscopy (PES) technique is the photoelectric effect. A photon hitting a surface can transfer its energy to an electron in the material. If the photon

\(^1\)A Gaussian function is of the form $\exp(-\alpha r^2)$. 

energy is sufficiently high, it can ionize the material. The kinetic energy of the ejected electron, the photoelectron, is given by the photoelectric law

\[ E_{\text{kin}} = h\nu - E_b, \]  

(8)

where \( h\nu \) is the energy of the incoming photon and \( E_b \) the binding energy relative to vacuum.

Hence, by measuring the kinetic energy of the outgoing electron, the binding energy can be determined. Electrons emitted from lower energy levels (core electrons) have higher binding energy than electrons emitted from the outer (valence) levels. The energies are quantized and each element has its characteristic set of energy levels. From the positions of the peaks in a PES spectrum, information about the element and energy level from which the electron was ejected can therefore be obtained. This information is available down to a few Å from the surface of the material. The surface sensitivity is due to the short electronic mean free path in the material. [18, 4]

The binding energy measured with PES is the difference between the initial (with \( N \) electrons) and the final state (with \( N - 1 \) electrons) energies. A core hole created due to photoemission will cause the system to relax and these effects are included in the final state energy. [4]

4 Molecular dynamics simulations

The solvation of \([\text{Ru(bpy)}_3]^{2+}\) and its interaction with different anions was investigated with MD simulations. The basis for the description of the interactions between the atoms was the individual force fields, comprising parameters like force constants and equilibrium quantities for each molecule type. For \([\text{Ru(bpy)}_3]^{2+}\), a force field was developed, whereas the other parameter sets required for the calculations were available in the literature.

In this section, the MD simulation details are given, beginning with the simulation setup. Thereafter, the general form of the force field is described, followed by the details of the parameter sets used. The last part treats the method for evaluating the \([\text{Ru(bpy)}_3]^{2+}\) force field.

4.1 Description of the simulations

Solutions consisting of \([\text{Ru(bpy)}_3]^{2+}\) and iodide and chloride, respectively, in water were simulated using the MDynaMix program [19]. For each anion type, the simulations were performed with two different compositions of the system:

The first system with iodide as anion consisted of one \([\text{Ru(bpy)}_3]^{2+}\), two iodide ions and 1720 water molecules, whereas the second solution consisted of eight Ru(II) complexes, 64 anions, 48 lithium ions (for charge neutrality) and 3200 water molecules.

The corresponding solutions with chloride consisted of one \([\text{Ru(bpy)}_3]^{2+}\), two chloride ions and 1730 water molecules and of eight Ru(II) complexes, 64 Cl\(^-\), 48 Li\(^+\) and 3200 water, respectively.

Also, a system with both anions present was simulated. The simulation cell contained eight \([\text{Ru(bpy)}_3]^{2+}\), 32 iodide, 32 chloride and 48 lithium ions and 3200 water molecules.

The simulations used periodic boundary conditions in all directions and were carried out at constant volume and temperature (NVT ensemble). The timestep of the MD algorithm was 2 fs. After equilibration, all simulations ran for at least 1.2 ns.

The solvation of the ions in water and the anion density near the ruthenium complex were investigated by computing radial distribution functions between the atom pairs of interest. The
number of solvent particles closest to the central atom was obtained by spherical integration of the RDF up to the first minimum. The three-dimensional density distribution was studied by calculating spatial distribution functions.

4.2 Description of the force field

The bonded contribution of the force field consists of three components: one describing the bonds, one describing the angles and one describing the dihedral angles.

All bonds except for the OH-bonds in the water molecules are modeled as harmonic oscillators:

$$U_{\text{bond}}(r) = k(r - r_0)^2,$$

(9)

where $k$ is the force constant and $r_0$ the equilibrium bond length. An alternative potential form is the more computationally costly Morse potential, which gives a better description of the vibrational structure. Near equilibrium, however, the harmonic potential is usually sufficiently accurate.

The angles are also described by a harmonic potential:

$$U_{\text{ang}}(\theta) = k_{\theta}(\theta - \theta_0)^2,$$

(10)

where $k_{\theta}$ is the force constant and $\theta_0$ the equilibrium angle. [12, 10]

There are two types of torsion potentials: dihedral angle potentials and improper torsions. The first depends on four consecutively bonded atoms. The torsional angle $\phi$ is calculated about the axis described by the two middle atoms and defined as being zero for a cis conformation. The improper torsions are defined by three atoms around a central atom [10]. Only dihedral torsions were included in the force field. The torsion potential is of the type

$$U_{\text{tors}}(\phi) = K_{\phi}(1 + \cos(M\phi - \Delta)),$$

(11)

where $K_{\phi}$ is the force constant, $M$ is the multiplicity and $\Delta$ the torsional angle at which the potential has a minimum.

The nonbonded interaction potential is the sum of the electrostatic and the van der Waals interactions. The electrostatic contribution is described by the Coulomb potential

$$U_{\text{el}} = \sum_{\text{nonbonded}} q_i q_j \frac{4 \pi \epsilon_0}{4 \pi \epsilon_0 r_{ij}},$$

(12)

summed over all atom pairs $ij$ that are in different molecules, or are separated by three or more bonds in the same molecule. $q_i$, $q_j$ are the partial atomic charges of atoms $i$ and $j$ respectively and $r_{ij}$ is the distance between them. $\epsilon_0$ is the vacuum permittivity. [12]

The van der Waals interactions can be expressed as the sum of a positive term describing the Pauli repulsion at short intramolecular distances and a long-range negative term due to dispersion. The model used for the van der Waals interactions is the Lennard-Jones potential:

$$U_{\text{LJ}} = \sum_{\text{nonbonded}} 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right].$$

(13)

The definition of a nonbonded atom pair is the same as in the electrostatic case. The Lennard-Jones parameters $\epsilon_{ij}$ and $\sigma_{ij}$ represent the potential depth and the (finite) interatomic distance at which the potential is zero, respectively. [11, 12]
4.3 Description of the models

In the MD simulations, the lithium, chloride and iodide ions were modeled as spheres with the effective atom radius $\sigma$ and a point charge $Q$ placed at the center. The force field parameters developed by Heinzinger [20] and listed in Table 1, were used.

For water, the Flexible Simple Point Charge (fSPC) model by Toukan and Rahman [21] was used. The H-H distance, 1.633 Å, is determined by a harmonic potential, whereas a Morse potential describes the OH-stretch (equilibrium bond length 1.0 Å) in this model. The electrostatic interactions are described by a Coulomb potential. The second of the two nonbonded terms is a Lennard-Jones potential between oxygen atoms in different molecules. The partial charges of the atoms and the Lennard-Jones parameters are found in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>$Q$</th>
<th>$\sigma$ (Å)</th>
<th>$\epsilon$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>1</td>
<td>2.37</td>
<td>0.149</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>-1</td>
<td>4.86</td>
<td>0.168</td>
</tr>
<tr>
<td>I$^-$</td>
<td>-1</td>
<td>5.40</td>
<td>0.408</td>
</tr>
<tr>
<td>H (water)</td>
<td>0.41</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O (water)</td>
<td>-0.82</td>
<td>3.17</td>
<td>0.650</td>
</tr>
</tbody>
</table>

A DFT-optimized gas phase geometry was used as the starting configuration of the $[\text{Ru(bpy)}_3]^{2+}$ molecule. The partial atomic charges for the complex were derived from the electrostatic potential, calculated at a number of grid points around the molecule. The grid was constructed of the van der Waals spheres around each atom, scaled by a factor. The calculation was carried out with Gaussian 03 [22] using the B3LYP method [23, 24] and the DGDZVP basis set for ruthenium and DGTZVP for all other atoms [25, 26]. Hereafter, these bases are denoted DGTZVP. The only vdW radius missing in the program was the one of ruthenium. This value was defined to 1.7 Å. [27]

The bond and angle parameters for pyridine were taken from the OPLS all-atom force field developed by Jorgensen and McDonald [28], while the bond, angle and torsion parameters for ruthenium were taken from a study by Moret et al. [29]. The remaining torsion parameters were taken from the AMBER/parm94 force field [30]. The only missing parameter was the N-C-C-N dihedral, for which the force constant was set to 4.0 kJ/(mol · rad$^2$).

The bond stretching parameters for $[\text{Ru(bpy)}_3]^{2+}$ are listed in Table 2 and the parameters for the angles and dihedral angles are found in Tables 3 and 4, respectively. The Lennard-Jones parameters are listed in Table 5. The parameters for hydrogen, carbon and nitrogen are taken from Moret et al. [29] and for ruthenium from Jorgensen et al. [28]. Standard AMBER nomenclature is used for the atom types.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$r_0$ (Å)</th>
<th>$k$ (kJ mol$^{-1}$ Å$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA - CA</td>
<td>1.400</td>
<td>1964</td>
</tr>
<tr>
<td>CA - NC</td>
<td>1.339</td>
<td>837.4</td>
</tr>
<tr>
<td>CA - HA</td>
<td>1.080</td>
<td>2022</td>
</tr>
<tr>
<td>Ru - NC</td>
<td>2.081</td>
<td>1120</td>
</tr>
</tbody>
</table>
Table 3: Angle bending parameters for [Ru(bpy)$_3$]$^{2+}$

<table>
<thead>
<tr>
<th>Angle</th>
<th>$\theta_0$ (deg)</th>
<th>$k_\theta$ (kJ mol$^{-1}$ rad$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA - CA - CA</td>
<td>120.0</td>
<td>264</td>
</tr>
<tr>
<td>CA - CA - NC</td>
<td>124.0</td>
<td>293</td>
</tr>
<tr>
<td>CA - NC - CA</td>
<td>117.0</td>
<td>293</td>
</tr>
<tr>
<td>CA - CA - HA</td>
<td>120.0</td>
<td>147</td>
</tr>
<tr>
<td>NC - CA - HA</td>
<td>116.0</td>
<td>147</td>
</tr>
<tr>
<td>Ru - NC - CA</td>
<td>123.5</td>
<td>433</td>
</tr>
<tr>
<td>NC - Ru - NC (cis)</td>
<td>91.1</td>
<td>340</td>
</tr>
<tr>
<td>NC - Ru - NC (trans)</td>
<td>180.0</td>
<td>103</td>
</tr>
</tbody>
</table>

Table 4: Dihedral torsion parameters for [Ru(bpy)$_3$]$^{2+}$

<table>
<thead>
<tr>
<th>Dihedral</th>
<th>$\Delta$ (deg)</th>
<th>$K_\phi$ (kJ mol$^{-1}$ rad$^{-2}$)</th>
<th>$M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA - CA - CA - CA</td>
<td>180</td>
<td>3.625</td>
<td>2</td>
</tr>
<tr>
<td>NC - CA - CA - CA</td>
<td>180</td>
<td>3.625</td>
<td>2</td>
</tr>
<tr>
<td>CA - CA - NC - CA</td>
<td>180</td>
<td>6.800</td>
<td>2</td>
</tr>
<tr>
<td>CA - NC - CA - HA</td>
<td>180</td>
<td>6.800</td>
<td>2</td>
</tr>
<tr>
<td>NC - CA - CA - HA</td>
<td>180</td>
<td>3.625</td>
<td>2</td>
</tr>
<tr>
<td>CA - CA - CA - HA</td>
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<tr>
<td>HA - CA - CA - CA</td>
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<td>3.625</td>
<td>2</td>
</tr>
<tr>
<td>HA - CA - NC - CA</td>
<td>180</td>
<td>0.000</td>
<td>2</td>
</tr>
<tr>
<td>NC - CA - HA - CA</td>
<td>180</td>
<td>0.000</td>
<td>2</td>
</tr>
<tr>
<td>CA - CA - CA - HA</td>
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</table>

Table 5: Lennard-Jones parameters for [Ru(bpy)$_3$]$^{2+}$

<table>
<thead>
<tr>
<th>Atom type</th>
<th>$\sigma$ (Å)</th>
<th>$\epsilon$ (kJ/mol)</th>
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<tr>
<td>CA</td>
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</tr>
<tr>
<td>NC</td>
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<td>0.711</td>
</tr>
<tr>
<td>HA</td>
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<td>0.126</td>
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<tr>
<td>Ru</td>
<td>2.963</td>
<td>2.343</td>
</tr>
</tbody>
</table>

4.4 Evaluation of the force field

In order to evaluate the force field, the B3LYP potential energy surface (PES) for a [Ru(bpy)$_3$]$^{2+}$ ion and a water molecule was scanned in one dimension, varying the O–Ru distance, and com-
pared with the force field potential energy surface. Two different B3LYP optimized geometries were analyzed: one where the starting geometry was taken from a simulation snapshot and one in which the water molecule was placed between two of the bipyridine groups, at a distance of 4.2 Å from the ruthenium atom. The potential energy surfaces for the basis sets DGTZVP [25, 26] and CEP-121G [31, 32, 33] were compared. Furthermore, the effect of basis set superposition error was investigated by doing a PES scan with counterpoise correction for the DGTZVP basis set.

The counterpoise corrected B3LYP PES for the (B3LYP/DGTZVP optimized) water dimer was calculated in a similar way, with the DGTZVP basis set. The hydrogen bond length and binding energy was hence obtained at the minimum. The purpose of the calculation was to give a feeling for the magnitude of discrepancies between the force field and B3LYP potential energy surfaces, if any.

Also, the solvation structure of the ruthenium complex obtained from MD simulations was compared with results from a previous study [8]. For this purpose, the radial distribution functions between ruthenium and oxygen were calculated, as well as the number of water molecules surrounding the ion.

5 Spectrum calculations

In the first part of the quantum chemical calculations of electronic spectra, the electronic structure of iodide and triiodide was computed at the DFT and RASSCF levels of theory. The purpose of the calculations was to identify and explain the components of the corresponding measured PE spectra. The results obtained with the two methods were compared.

In the second part, DFT was used for calculations of the electronic structure of [Ru(bpy)$_3$]$_{2+}$, with focus on a possible interaction with iodide. The computed density of states was compared with the PE valence spectrum of [Ru(bpy)$_3$]$_{2+}$.

The computational details are given below. For a general description of the quantum chemical methods used, see Section 3.2.

5.1 Iodide/triiodide

The calculations of the electronic structure of gas-phase iodide and triiodide at the 3$d$ and 4$d$ levels and at the valence (5$s$/$p$) level were essentially carried out with the StoBe [34] and Molcas [35] programs. The results were compared with PE spectra of iodide and triiodide in aqueous solution, measured at the core levels. For iodide, calculations of the solvated ion were also performed.

The geometry of triiodide was optimized with different methods and basis sets, in order to compare the bond lengths thereby obtained. B3LYP [23, 24] calculations were performed with the Gaussian 03 software [22], using a triple-zeta valence basis including polarization functions [25, 26] and an effective core potential (ECP) basis set [36, 37, 38, 39], respectively. The other methods used are described below.

With Gaussian, excited states of the triiodide molecule were also calculated. The information about allowed electronic transitions was used for estimating effects related to photoionization.
5.1.1 StoBe calculations

The StoBe calculations of triiodide were performed with the pure DFT method BP86 [43, 44]. For the geometry optimization of triiodide, two different basis sets were used: a double-zeta valence basis set with polarizing functions [25] and an effective core potential [45].

The binding energies of the iodide and triiodide ions, calculated with StoBe, were equal to the negative Kohn-Sham orbital energies. The iodine atoms were represented by the double-zeta valence basis in these calculations. The density-of-states (DOS) curves were generated by Gaussian broadening of the computed 3$d$, 4$d$ and 5$sp$ energy levels. Spin-orbit interactions were not calculated.

An attempt to estimate the solvation shift of iodide was made by calculating the valence orbital energies of the the naked ion and of the ion solvated in clusters of 7 and 31 water molecules, respectively. The cluster geometries were taken from MD simulation snapshots (Section 4) and the ECP basis set was used to describe the atoms.

5.1.2 Molcas calculations

With Molcas, the calculations were performed at the RASSCF level, using a relativistic all-electron basis set [42]. Relativistic effects, including spin-orbit coupling, were calculated. The projection of the spin (the $M_s$ quantum number) is not defined for the RASSCF wave functions; the spin-orbit interaction between these spin-free states was computed in a second step [46]. The gas-phase geometry was also optimized using this method.

The binding energies were calculated as the difference between the initial ground state energy of the ion and the energies of the possible final states with one electron removed from an 4$d$, 5$s$ or 5$p$ orbital (= the active space). For the gas-phase iodide ion, one hole was allowed in the 4$d$ and 5$s$ orbitals. Given that there were 18 electrons in the active space of the initial singlet state, all possible configurations in the three 5$p$ orbitals were taken into account. The same restrictions applied for the final doublet state, with 17 electrons in the active space.

The triiodide ion is also a singlet in its ground state. As in the iodide calculation, one hole was allowed in the orbitals constructed of the atomic 4$d$ and 5$s$ orbitals. The CAS space consisted of the eight highest occupied molecular orbitals, corresponding to the atomic 5$p$ orbitals, with the exception of the lowest unoccupied molecular orbital (LUMO), constructed out of them.

In addition to the gas-phase calculation, solvation effects on the iodide ion were investigated by performing a PCM calculation of the ion in water.

5.2 $\text{[Ru(bpy)$_3$]}^{2+}$

Three different DFT calculations of the $\text{[Ru(bpy)$_3$]}^{2+}$ molecule were carried out: for the DFT-optimized gas-phase complex, for the complex in water and for the complex and an iodide ion in water.

The geometry of the $\text{[Ru(bpy)$_3$]}^{2+}$ molecule was taken from a simulation snapshot of the ruthenium complex and iodide ions solvated in water (Section 4) and included the water molecules closest to the complex. The geometry in the calculation of the dye, iodide and water was in other respects identical to this one, but included also the closest iodide ion.

The molecular orbitals were calculated with the StoBe package [34], at the gradient-corrected DFT level, using the BP86 [43, 44] functional. For ruthenium and iodide, combined Dolg basis sets and effective core potentials [45, 47] were used. The carbon, nitrogen and oxygen atoms were
described by valence basis sets combined with effective core potentials [48, 49] and the hydrogen with a polarized valence triple-zeta basis set [25].

The calculated DOS spectra were then compared with the experimental valence spectrum of [Ru(bpy)$_3$]$^{2+}$ in aqueous solution.

5.3 Experiments

The PES measurements were carried out at the synchrotron facilities MAX-lab in Lund and BESSY in Berlin. The 3$d$ level was measured with the photon energy 725 eV. A sample containing I$^-$ as anion and one with I$^-$ and I$_3^-$ in water were studied.

Triiodide 4$d$ in ethanol was measured with 100 eV photon energy. The 4$d$ level of I$^-$ in water was studied using the photon energy 200 eV [50].
6 Results and discussion

The results from the previously described calculations described will be shown and discussed in this section. Two calculation areas are essentially covered in this thesis: MD simulations and quantum chemical calculations of electronic spectra. The calculated spectra are compared with experimental PE spectra.

The purpose of the MD simulations was to investigate the hydration structure of $[\text{Ru(bpy)}_3]^{2+}$ and its interaction with iodide and chloride at a molecular level. Development of a force field for the $[\text{Ru(bpy)}_3]^{2+}$ molecule and examination of the solvation structure of the separate monatomic ions were important parts of this.

The spectrum calculations consisted mainly of two parts. First, calculation of the electronic structure of $[\text{Ru(bpy)}_3]^{2+}$. Second, calculation of electronic spectra of iodide and triiodide. The results are basically discussed in the order stated here.

6.1 Evaluation of the $[\text{Ru(bpy)}_3]^{2+}$ force field

The forces on the individual atoms, calculated for each timestep in an MD simulation, are totally dependent on the force field used. A natural way of evaluating the choice of force field is to compare the results it yields with results from other calculations. The problem of evaluating the force field for $[\text{Ru(bpy)}_3]^{2+}$, used in the MD simulations in this work (Section 4.4) was approached in the two ways described below. The first part is a comparison between the potential energy curves calculated using the force field for $[\text{Ru(bpy)}_3]^{2+}$ with curves obtained from quantum chemical calculations. The second part compares a radial distribution function from an MD simulation using this force field with one from a previous study.

6.1.1 Potential energy surfaces

The potential energy at different distances between a water molecule and a ruthenium complex had its minimum at an O-Ru separation of between 5 and 6 Å, depending on the geometry and type of calculation. The equilibrium distance was shorter for geometry A than for geometry B (Fig. 3).

Different calculations gave potential depths between 24 kJ/mol and 38 kJ/mol; the minimum energy for the last geometry was lower than for the first one. All the potential energy curves (Fig. 4–6) have been normalized with respect to the energy at infinite distance between the water molecule and the ruthenium complex.

For both geometries, the equilibrium distance was about 0.2 Å longer for the force field potential energy curve than for the B3LYP/DGTZVP potential curve (Fig 4). The force field potentials were deeper than the B3LYP potentials and the energies at the minima differed more for geometry A, 3 kJ/mol, than for geometry B, 1 kJ/mol.

When basis set superposition error (BSSE) correction was included in the calculation using the DGTZVP basis set (geometry B), the equilibrium distance increased (Fig. 5). The distance between the molecules at minimum energy was then 0.1 Å shorter than the corresponding distance obtained from the force field calculation. The energy at the minimum increased; the energy difference between the force field minimum and the BSSE corrected B3LYP calculated minimum was 2 kJ/mol.

The equilibrium distance obtained with different basis sets was the same for all calculations; somewhat shorter than the force field equilibrium distance. The depth of the potential well,
Figure 3: The two different geometries, for which the potential energy curves were scanned.

Figure 4: B3LYP and force field potential energy surfaces, respectively, for the two different geometries.

however, differed significantly with the basis set used.

In Fig. 6, the (counterpoise corrected) B3LYP potential energy surfaces calculated with the basis sets DGTZVP and CEP-121G, are shown for geometry B. For comparison, the force field potential energy surface is also drawn in the figure. Of these two B3LYP potential energy curves, the minimum potential energy for the force field agreed the best with the potential corresponding to the DGTZVP basis set. The difference between the minimum energies for the two B3LYP potentials was almost 10 kJ/mol.

The minimum distance between the water oxygen and the complex is basically determined by the radii of the carbon and nitrogen atoms. A better agreement of the force field equilibrium
distance with quantum chemical calculations could therefore be expected by decreasing the values of the Lennard-Jones parameter $\sigma$ for these atom types. Yet, the discrepancy between the QC and FF equilibrium $O$–$Ru$ distances is only one tenth of the B3LYP/DGTZVP hydrogen bond length, calculated for the water dimer ($O$–$H$ equilibrium distance: 1.9 Å). Even though the effective size of the complex appears somewhat too large, we might hence conclude that the difference has minor influence on how close to the complex other atoms may come.

Similarly, the force field potential depth could be fit to the quantum chemical potential by
modification of the value of $\epsilon$. In this case it is evident that the choice of basis set is important for the outcome. The B3LYP/DGTZVP calculated hydrogen bond strength was slightly below 20 kJ/mol. As for the $[\text{Ru(bpy)}_3]^{2+} - \text{H}_2\text{O}$ cluster, the choice of basis set can be expected to affect the results much, which makes it difficult to evaluate the present value of $\epsilon$ in this way. A better basis set than the DGTZVP should probably be used in order to estimate if the force field serves as a good model for the atomic interactions.

6.1.2 Radial distribution functions

The radial distribution function between ruthenium and water oxygen have recently been calculated in a density functional molecular dynamics (DFMD) study at the PBE/TZV2P level of theory [8]. The corresponding RDF from an MD simulation, where the force field described above was used, was compared with this result (Fig. 7). The first solvation shells appeared at the same Ru–O distance, which seems to confirm that the force field parameter $\sigma$ is reasonably accurate. The coordination numbers differed significantly: for the MD simulation, the number

![Figure 7: Radial distribution function between ruthenium and oxygen from MD (orange) and DFMD (black) [8] simulations.](image)

of water molecules integrated up to the first minimum was 12, in contrast to 7 in the DFMD simulation. Integration of the RDF from the simulation using the force field up to the minimum in the DFMD radial distribution function resulted in 9 water molecules. With the force field used in the simulations of this work, the water molecules seem less ordered around the complex, therefore coming closer to each other.

6.2 Solvation of lithium, chloride and iodide ions in water

Integration of the radial distribution functions between lithium ions in aqueous solution and the water oxygen and hydrogen (Fig. 8) showed that the first solvation shell around the lithium ion consisted of five water molecules (5.4 on average). These were oriented with the more electronegative oxygen atoms towards the cation. Due to the positive net charge on the outside of the first shell, a second, more diffuse, shell was formed at 4–5 Å from the ion.
Figure 8: Radial distribution functions between lithium and water oxygen (left) and lithium and hydrogen (right).

For the anions, chloride and iodide, the positive hydrogen ends of the water molecules in the solvation shell were facing the ion. (Fig. 9). The number of water molecules in the first solvation shell was approximately the same for both anions: seven water molecules surrounded the chloride ion, whereas there was seven or eight water molecules around the iodide ion. However, the water molecules can come closer to the smaller chloride ion (Fig. 9). We can therefore expect the chloride ion to hold the water molecules more strongly.

Figure 9: Radial distribution functions between the anions (chloride and iodide) and water oxygen (left) and between the anions and hydrogen (right).

6.3 $[\text{Ru}(\text{bpy})_3]^{2+}$

The symmetry of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex (Fig. 2) should affect the structure of its hydration shell. In order to investigate this, the radial and spatial distribution functions between the central atom of the complex and the oxygen and hydrogen atoms in the water molecules are analyzed below. Another question of interest is how different anions are distributed around the Ru(II) complex in water solution. In Section 6.3.2, the trajectory analyses from MD simulations with iodide and/or chloride as anions are therefore discussed.
6.3.1 Solvation of $[\text{Ru(bpy)}_3]^{2+}$

Ru–water radial distribution functions, calculated from MD simulations including $[\text{Ru(bpy)}_3]^{2+}$ in aqueous solution, showed no difference for simulations with different counterions (iodide and chloride). The radial distribution function had its first maximum at 5–6 Å from the Ru atom. The first peak in the ruthenium–oxygen RDF appeared at a somewhat shorter distance than the corresponding peak in the ruthenium–hydrogen RDF. This shows that the water molecules in the solvation shell around a $[\text{Ru(bpy)}_3]^{2+}$ cation mostly orient themselves with the oxygen atoms pointing towards the complex center.

At 8 Å, a second maximum in the RDF was seen. Here, also, the oxygen atoms were the closest to the central atom, with the hydrogen atoms directed outwards. The number of water molecules in the first solvation shell, calculated as the number of oxygen atoms integrated up to the first minimum, was 12.

Spatial distribution functions can give an idea of how the solvent molecules are actually arranged in space around the solute. The spatial distribution functions described below were calculated from the same MD simulations as the previously mentioned radial distribution functions. The spatial distribution functions between ruthenium and water oxygen and hydrogen, respectively, showed that the water molecules in the first solvation shell aligned themselves in a symmetrical pattern between the bipyridine ligands. The arrangement of water in the first shell (and some of the second) around the $[\text{Ru(bpy)}_3]^{2+}$ molecule is shown in Fig. 10. The first subfigure only shows the oxygen distribution (red in the figure), whereas the second subfigure also shows the hydrogen, distributed on the outside of the oxygen, in agreement with the radial distribution functions. In Fig. 11, a $[\text{Ru(bpy)}_3]^{2+}$ ion surrounded by water molecules corre-

Figure 10: Spatial distribution of water around a $[\text{Ru(bpy)}_3]^{2+}$ molecule. Left: oxygen distribution seen along the $C_3$ axis. Right: oxygen and hydrogen seen along the plane perpendicular to the $C_3$ axis.

sponding to the first and some of the second solvation shell, is shown. The picture is a snapshot from a molecular dynamics simulation of the Ru complex and iodide ions in water, represented with vdW spheres.

The water molecules in the second solvation shell around the $[\text{Ru(bpy)}_3]^{2+}$ molecule were arranged over and across the spacings of the first shell. Fig. 12 shows the spatial distribution of water in the second solvation shell, for successively decreasing intensity of the contour plot.
Figure 11: An iodide ion (green) and water molecules in the first and some of the second hydration shell around a $[\text{Ru(bpy)}_3]^{2+}$ ion, seen along the molecular $C_3$ axis. (Snapshot from MD simulation.)

Figure 12: Spatial distribution of oxygen in the first and second solvation shells around the $[\text{Ru(bpy)}_3]^{2+}$ ion.

6.3.2 Anion distribution

The distance at which the radial distribution functions between the central atom in the ruthenium complex and the other ions had their maxima and minima showed no dependence on the ion concentration or on the presence of other solutes. For systems with low ion concentration, however, the values of the Ru–anion radial distribution functions appeared to be very sensitive to the simulation time. The effect was particularly apparent for the spatial distribution functions – it was almost impossible to extract usable information from the contour plots, even for very long simulation times, if the solution contained just a few ions. An increase in the number of anions and Ru complexes improved the statistics much. An alternative way of achieving better statistics in the radial distribution functions, could have been by defining multiple equivalent coordinate systems within the complex when performing the trajectory analysis.

The radial distribution functions in Fig. 13 were calculated from simulations of solutions containing $[\text{Ru(bpy)}_3]^{2+}$ and one type of anions. The RDF between ruthenium and iodide (left subfigure) had two maxima: one at the Ru–I distance 7 Å and one at 8.5 Å. The two iodide peaks were positioned just outside the first and second water maxima with respect to the center of the Ru complex. In the Ru–Cl radial distribution function (right subfigure), there was only one maximum, outside the second water peak. Fig. 14 shows that the iodide ions indeed arranged themselves outside the first and second hydration shells around the ruthenium complex, whereas
Figure 13: Radial distribution functions between water oxygen (red) and hydrogen (gray) and ruthenium and between iodide and ruthenium (left, green line) and chloride and ruthenium (right, blue line).

The chloride ions were found only outside the second water shell.

Figure 14: Distribution of water oxygen atoms (red) and iodide (green) and chloride (blue) ions around a \([\text{Ru(bpy)}_3]^{2+}\) molecule.

The atom sizes set the lower limit for the distance between the ruthenium atom and the anions: 5.4 Å. Although it is possible for the chloride ion to get equally close to the center of the Ru complex as for the iodide ion (Fig. 15), the value of the Ru–Cl radial distribution function was very low inside the second hydration shell. From the simulation of an aqueous solution containing both iodide and chloride ions it became clear that the second iodide maximum and the chloride maximum occur at the same distance from the \([\text{Ru(bpy)}_3]^{2+}\) center: directly outside the second water shell. An explanation of the different behavior close to the Ru complex can be found from the fact that the iodide ion does not bind the water molecules as tight as the chloride ion (Section 6.2). Therefore, the iodide ion can enter between the bipyridine ligands rather naked, whereas the chloride ion and its hydration shell will not fit between the ligands.

One of the reasons that iodide works so well for regeneration of the oxidized dye might hence be that it comes sufficiently close for the reaction

\[
[\text{Ru(bpy)}_3]^{3+} + 2\text{I}^- \rightarrow [\text{Ru(bpy)}_3]^{2+} + \text{I}_2
\]  

(14)

to take place. A natural approach, in order to investigate this further, would be MD simulations.
Figure 15: Radial distribution functions between the central atom in the \([Ru(bpy)_3]^{2+}\) molecule and water oxygen and hydrogen, iodide and chloride, respectively.

of iodide ions and the oxidized dye in water. This requires that a force field for the \([Ru(bpy)_3]^{3+}\) molecule is developed.

6.4 Triiodide

The geometry optimization of the triiodide ion in the gas phase showed that the molecule has a linear \(D_{\infty h}\) geometry. Different calculations gave equilibrium bond lengths between 2.97 Å and 3.15 Å, as shown in Table 6. Here, the significance of relativistic effects when dealing with the heavy iodine atom is clearly seen; the relativistic calculation gave a much shorter bond length than the DFT calculations with different basis sets.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Bond length (Å)</th>
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<tr>
<td>BP86 /AE (DZVP)</td>
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</tr>
<tr>
<td>BP86 /ECP (Dolg)</td>
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<tr>
<td>B3LYP /AE (TZVP)</td>
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</tr>
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<td>B3LYP/ECP (LANL2DZ)</td>
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</tr>
<tr>
<td>Rel. (Molcas) /ANO-RCC</td>
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</tr>
</tbody>
</table>

Table 6: I-I bond length in the \(I_3^-\) ion.

The value 2.97 Å of the I-I bond length, obtained in the relativistic geometry optimization with Molcas, was used in all the Molcas calculations of the gas-phase molecule.

In all the calculations, the major part of the electron density was located around the terminal atoms. The Mulliken partial charge on each terminal atom was between -0.4e and -0.7e, depending on the method. Correspondingly, the charges of the central iodine ranged between -0.1e and +0.4e. The terminal atoms were the most negative in the relativistic calculation.
6.4.1 Core-level energies

The difference in the distribution of the electron density was seen as a distinct separation between the contributions from the terminal and the central atoms in the $3d$ and $4d$ spectra of gaseous triiodide. The transfer of valence electrons from the central atom to the terminal sites gives rise to a lowering in core binding energy of the terminal atoms. This was seen as a peak at lower orbital energy (higher binding energy), corresponding to the central atom, and one at higher orbital energy, corresponding to the two terminal atoms. The energy difference between the two peaks was 0.75 eV in the DFT calculated $3d$ spectrum (Fig. 16).

Figure 16: DOS spectrum of triiodide ($3d$), showing the partial density of states (PDOS) of the central and terminal atoms, respectively.

Molecular orbitals oriented differently with respect to the molecular axis differed somewhat in energy, as seen from Fig. 17. The $\delta$ orbitals were the highest and the $\sigma$ orbitals the lowest. This is due to the fact that the electrons in atomic $d$ orbitals oriented along the internuclear axis are more affected by the nuclear charge, than those in orbitals aligned perpendicularly to the axis. The influence from the nuclei is larger on the electrons in orbitals centered on the central iodine than on the terminal sites. This was seen as a larger broadening of the peak corresponding to the central atom.

The experimental $3d$ spectra of $I^-$ and $I_3^-$ was measured at a photon energy of 725 eV [50]. Due to the large spin-orbit splitting at this level – the $3d_{5/2}$ and $3d_{3/2}$ peaks were separated by 12 eV in the experimental spectrum [51] – the $3d_{5/2}$ peak could be compared with the spin-free DOS spectrum of triiodide (Fig. 18). The highest peak in the experimental spectrum contained a contribution from iodide $3d_{5/2}$ as well as from triiodide: the peak in the iodide spectrum was positioned close to the most intense peak in the iodide/triiodide spectrum, at a somewhat lower binding energy.

In the experimental spectrum of iodide and triiodide in water, the two main peaks were separated by 1.1 eV. The corresponding splitting in the DFT-calculated spectrum was smaller: 0.8 eV. At 5 eV higher binding energy than the most intense peak, a smaller peak was observed in the experimental triiodide/iodide spectrum. This shake-up peak was absent in the theoretical triiodide spectrum.

In the calculation of the theoretical spectrum, all final state effects were neglected. A theoretical spectrum with better agreement with experiment could be obtained by performing a
Figure 17: PDOS spectrum of different molecular orbitals in triiodide ($3d$).

Figure 18: PE spectrum ($3d$) of triiodide and iodide (red line) and of iodide (blue line) in water.

RASSCF calculation, instead of letting the eigenenergies of the Kohn–Sham orbitals correspond to the binding energies. By allowing excited configurations in the wave function, shake-up effects could be accounted for. Treatment of the shake-up process is discussed further for the $4d$ level, below.

Another limitation is that the triiodide spectrum was computed for the gas-phase molecule, whereas the experimental spectrum was measured of the ion in water solution. Due to electrostatic stabilization, the binding energy of the solvated anion will be shifted towards higher binding energies. We see that the peaks in the experimental spectrum were shifted 7.5 eV with respect to the calculated gas-phase spectrum. Therefore, it would be interesting to compute the chemical shift of triiodide. This could be done by performing a PCM calculation and compare the results with the energy obtained from a calculation of the bare ion.

Also, the polarizing effect of different solvents on the trioxide ion could be studied with PCM. It is possible that different solvents would influence the charge distribution of $I_3^-$ differently. In that case, the observed terminal/center splitting could be expected to differ, depending on the
For 4d, spectra were computed with Molcas, as well as with StoBe. The contributions from different molecular orbitals were more well-separated in the 4d spectrum than for the lower lying 3d orbitals. The values of the sigma/pi/delta splitting of the 4d level, obtained in the Molcas and the StoBe calculations, were approximately the same (Table 7). However, the difference in binding energy between the terminal and central peaks differed more: 1.0 eV calculated with Molcas and about the same as for 3d, 0.8 eV, in the StoBe spectrum. This is in agreement with the greater difference in charge density on the terminal and central sites obtained in the relativistic calculation. It is important to note that no spin-orbit coupling was included in the calculations at this stage.

The natural question to ask next, would be whether the overlap between the 4d orbitals on the terminal atoms is also of significance for the spectrum. If the overlap would be sufficiently large, bonding combinations of the orbitals would raise the binding energy, whereas orbitals combined in an antibonding manner would be destabilized, leading to a lower binding energy.

The largest overlap, and hence the largest splitting, could then be expected for combinations of atomic orbitals oriented along the molecular axis - the σ orbitals. Similarly, the smallest splitting should be observed for orbitals oriented perpendicularly to the axis (δ orbitals). (Fig. 19.)

![Figure 19: Bonding combinations of 4d orbitals on the terminal atoms of triiodide.](image)

A very small ($10^{-5} - 10^{-3}$ eV) splitting of the levels corresponding to photoemission from the terminal atoms was indeed observed in the Molcas calculation. Of these, the splitting of the Σ states was the most significant, and the Δ splitting the smallest. This seems to confirm, that with a sufficiently high resolution, a fine structure, due to the overlap between 4d orbitals, could be expected to be observed in the experimental $I_3^-$ spectrum.

The splitting of the 4d level discussed here is shown in Fig. 20 in the next section.
6.4.2 Spin-orbit coupling

An overview of the splitting of the 4d level of triiodide is given in the energy level diagram in Fig. 20. First, the terminal/center splitting due to the difference in electron density on the different sites is shown. Next, the splitting due to the difference in nuclear charge felt by the electrons in orbitals with different orientation with respect to the internuclear axis is shown. The gerade/ungerade splitting due to the bonding or antibonding character of the orbitals on the terminal sites is also indicated, listing the spin-free states with their parity included. To the right in the figure, the energies of the spin-orbit states, obtained by computing the spin-orbit interaction between the spin-free states, are shown.

With Molcas, values of the spin-orbit splitting between 1.59 eV and 1.72 eV were obtained. The experimentally determined value is 1.7 eV [50].

Figure 20: Energy level diagram illustrating the splitting of the 4d level of triiodide. The energies of the states of the neutral molecule are given relative to the singlet ground state of $I_3^-$ (eV).
In Fig. 21, the experimental PE spectrum of I$_3^-$ solvated in ethanol is shown, together with the theoretical spectrum computed with RASSCF, including spin-orbit coupling. The most intense peak in the theoretical spectrum has been aligned with the corresponding peak in the experimental spectrum.

The relative positions of the peaks (1)–(3) in the calculated spectrum were in good agreement with the experimental main peaks and the assignment given in Fig. 20 should hence be appropriate for the experimental spectrum. As seen from Fig. 20, the peak with the highest intensity (1) corresponds to photoionization from the terminal sites. Due to spin-orbit splitting, a second peak from the terminal iodine appeared at about 1.6 eV higher binding energy, in the middle main peak (2). The peak denoted (2) also contains a contribution from the central iodine, at the low binding energy side of the peak. The least intense peak (3), finally, is the second line resulting from ionization from the central atom.

The creation of a core hole, due to photoemission, will cause the electrons in the outer shells to relax. If the electrons then have time to interact with the departing photoelectron, the photoelectron can transfer energy to the system. Thereby, one of the valence electrons may become excited. The kinetic energy of the detected photoelectron will thus be lower and result in a line at higher binding energy. To a first approximation, the photoionization can be assumed to happen so fast that no relaxation takes place during the ionization [52].

An apparent difference between the computed and the experimental spectra was the shake-up satellite observed at almost 5 eV higher binding energy than the most intense of the main peaks in the experimental spectrum. This feature was completely absent in the theoretical spectrum, since the calculation was restricted to include only occupied orbitals. In order to account for
shake-up effects, the RASSCF calculation could be extended to allow configurations with one electron in higher lying orbitals. The energy of the shake-up satellite would then be given as the energy difference between the final ionized state, with a core hole and an excited valence electron, and the initial ground state with all orbitals doubly occupied. An estimate of the shake-up energy, was obtained in a B3LYP excited state calculation with Gaussian. The lowest excitation energy with significant transition probability was 4.6 eV, corresponding to a transition from the highest occupied valence \( \sigma \) orbital to the LUMO (\( \sigma_u \)). Hence, a possible shake-up peak could be expected at 4.6 eV to the low-binding energy side of a main peak. This result agrees reasonably well with the position of the satellite, with respect to the most intense terminal peak, in the experimental spectrum.

Another significant deviation between calculation and experiment was in the peak intensity ratios. In the calculated spectrum, the ratio between the heights of peaks (1) and (2) was higher than in the experiment. The reason for this might be that the kinetic energy of some of the photoelectrons ejected from the terminal atom (corresponding to peak (2)) was reduced, due to shake-up effects, leading to a lower intensity of the main peak. An important limitation of the calculated intensities is that all states were assumed to contribute to the intensity with equal weight. No regard was taken to the fact that the probability for photoemission from a certain MO actually depends on the orbital character.

More accurate results should be obtained if using multireference perturbation theory, e.g. RASPT2. Also, solvation effects on the spectrum should be investigated, as previously discussed for 3d.

### 6.4.3 The valence level

The Molcas calculated 5sp spectrum of gas-phase I\(_3^-\) was built up by eleven discrete energy levels, originating from eight spin-free states. In the 5s part of the spectrum, three peaks appeared at the binding energies 17.22, 19.72 and 20.63 eV, respectively. These states correspond to photoionization from each of the three \( \sigma \) orbitals, mostly of 5s character, shown in Fig. 22.

![Molecular orbitals of triiodide, composed of 5s orbitals.](image)

Figure 22: Molecular orbitals of triiodide, composed of 5s orbitals.

No spin-orbit splitting occurred for these \( \Sigma \) states (\( M_L = 0 \)). The spin-free, doubly degenerate, \( \Pi \) states in the 5p part of the spectrum were split into two levels with \( \Omega = 1/2 \) and \( \Omega = 3/2 \) (Fig. 23). The calculated spin-orbit splitting was 0.6–0.7 eV.

The calculated 5p spectra of gas-phase iodide and triiodide are shown in Fig. 24. The I\(_3^-\) molecular orbitals, composed of 5p orbitals are shown in Fig. 25. An unpaired electron in one of these, due to photoionization from I\(_3^-\), gives rise to the states described above. The electron configuration of the three spin-free states at lowest binding energy: \( {}^2 \Sigma_g \), \( {}^2 \Pi_u \) and \( {}^2 \Pi_g \) is shown in Fig. 26.
<table>
<thead>
<tr>
<th>[eV]</th>
<th>$^2\Sigma_g$ (1)</th>
<th>[eV]</th>
<th>$^2\Sigma_{1/2,g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.56</td>
<td></td>
<td>4.47</td>
<td></td>
</tr>
<tr>
<td>5.10</td>
<td>$^2\Pi_u$ (2)</td>
<td>4.77</td>
<td>$^2\Pi_{1/2,u}$</td>
</tr>
<tr>
<td>6.02</td>
<td>$^2\Pi_g$ (2)</td>
<td>5.36</td>
<td>$^2\Pi_{1/2,u}$</td>
</tr>
<tr>
<td>7.19</td>
<td>$^2\Pi_u$ (2)</td>
<td>5.73</td>
<td>$^2\Pi_{3/2,u}$</td>
</tr>
<tr>
<td>8.38</td>
<td>$^2\Sigma_u$ (1)</td>
<td>6.40</td>
<td>$^2\Pi_{1/2,g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.91</td>
<td>$^2\Pi_{3/2,u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.47</td>
<td>$^2\Pi_{1/2,u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.43</td>
<td>$^2\Sigma_{1/2,u}$</td>
</tr>
</tbody>
</table>

Figure 23: Energy level diagram of the doublet states of $\text{I}_3$, obtained by removing an electron from the occupied 5s and 5p orbitals of $\text{I}_3^-$. Left: spin-free states. Right: spin-orbit states The energies are given relative to the ground state of $\text{I}_3^-$. 

![Image](image_url)

Figure 24: RASSCF+SO calculated PE spectrum of triiodide and iodide 5p.

The assignment of the valence spectrum of gas-phase $\text{I}_3$ discussed here might be helpful in the analysis of experimental photoelectron valence spectra of triiodide. In order to further account for electron correlation, a RASPT2 calculation should be performed. Furthermore, the electronic...
structure of the triiodide ion in solvents with different polarities should be investigated.

In the electrolyte in the Grätzel cell, iodide ions are present, as well as triiodide. Therefore, the shift of $I^-$ with respect to $I_3^-$ is of interest. The relative energies in the liquid phase have not been calculated here. In the gas-phase RASSCF+SO calculation, the $5p_{3/2}$ peak was shifted 1.7 eV towards lower binding energies, with respect to the most intense peak in the triiodide spectrum (Fig. 24). For reliable values of the relative energies, the calculations should be carried out at the RASPT2 level, however. The spin-orbit splitting of iodide $5p$ in the gas phase, calculated with the same method as the $I_3$ spectrum, was 1.0 eV. The iodide-triiodide shift in different liquid samples might hence be a subject for future studies.
6.4.4 Solvation effects on iodide

The electronic structure calculations described above were all performed for single molecules, whereas spectra of liquid samples were measured in the experiments. Due to electrostatic stabilization, the binding energy of an anion can be expected to increase when solvated, while on the contrary the binding energy of a solvated cation should decrease with respect to the gas phase.

In order to investigate the chemical shift of $I^-$ due to solvation in water, the 5s and 5p binding energies of gas-phase iodide, iodide solvated by seven water molecules and by 31 water molecules were compared. The binding energies were approximated with the Kohn-Sham energies. In this calculation, spin orbit coupling was not accounted for. Therefore, the spectra had only two components: 5s and 5p (Fig. 27(a)). From the figure it is clear that the energy is shifted towards higher binding energies with increasing size of the water cluster. The binding energy increased with 3.0 eV (for 5p) for the iodide ion solvated in seven water molecules. When solvated in the larger cluster, the shift was 4.1 eV. No value of the shift for the ion in bulk solution was obtained hereby. Judging from the computed spectra, it does not seem unreasonable to assume that the DFT calculated solvation shift would converge to a value between 4 and 5 eV for a successively increasing number of water molecules surrounding the ion. The experimental value is only 3.5 eV [53].

The difference in binding energy of the iodide ion in the gas phase and in the polarizable continuum model was also computed (Fig. 27(b)) with RASSCF+SO. The calculated shift was considerably smaller than in the DFT calculation: 2.7 eV.

![Figure 27: Binding energies of the bare iodide ion and of the ion in water.](image)

The most attractive choice of these two, in order to compute the chemical shift for iodide in different environments, would be the PCM method, taking relativistic effects into account also. Increasing the number of water molecules in the cluster model increases the computational cost rapidly and makes an individual treatment of the solvent molecules unmanageable.

Continuing, the electronic structure of $I_3^-$ in different solvents should be calculated. The shift in binding energy with respect to $I^-$ might then be calculated, which would be important for the understanding of the experimental spectra.

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6.5 Electronic structure of $[\text{Ru(bpy)}_3]^{2+}$

DOS spectra were computed for $[\text{Ru(bpy)}_3]^{2+}$ in the gas phase, for the ruthenium complex in water and for the complex and an iodide ion in water. The geometry of the solvated complex, taken from an MD simulation snapshot, included 11 water molecules. The geometry used in the calculation with iodide and water was the same as in the water calculation, with the addition of an iodide ion – partly covered with water – in the outer range of the cluster.

In order to investigate if there were differences in the $[\text{Ru(bpy)}_3]^{2+}$ density of states for the gas-phase and solvated complex and when close to an iodide ion, the ruthenium and iodide (when present) contributions to the density of states was calculated. The Ru PDOS were close to identical in the three calculations (Fig. 28). At the position of the iodide $5p$ peak, however, there appeared to be a very slight contribution from ruthenium only from the calculation including iodide, whereas the HOMOs in the other two calculations were well below this level.

![Figure 28: Ru-PDOS spectrum. (a) represents the calculation of $[\text{Ru(bpy)}_3]^{2+}$, iodide and water, (b) of $[\text{Ru(bpy)}_3]^{2+}$ and water and (c) of gas-phase $[\text{Ru(bpy)}_3]^{2+}$. The green line shows the I-PDOS in calculation (a). The Ru $4d$ peaks in (a) and (b) are aligned with the gas-phase $4d$ peak.](image)

The PDOS spectrum of all the atoms in the complex (with the exception of hydrogen) showed that one of the orbitals of the Ru complex was indeed occupied only in the presence of iodide (Fig. 29). The orbital in question is shown in Fig. 30.

The small number of water molecules surrounding the ions is an obvious limitation of the calculation. The Ru $4d$ peak shifted 0.29 eV to lower binding energies when solvated in a cluster of 11 water molecules. Any conclusion about the electrostatic stabilization of the Ru(II) complexation in bulk solution from this is uncertain, due to the small cluster size.

It is evident from Fig. 28–29 that the relative positions of the Ru(II) complex and the I PDOS spectra – in particular the $5p$ peak of $I^-$ – are important when considering possible molecular overlaps between iodide and $[\text{Ru(bpy)}_3]^{2+}$. The geometry of the solvated ions, where especially the iodide ion was partly naked, should therefore be replaced with one where the ions are surrounded by more water, in order to improve the calculation. An attempt to do so,
Figure 29: PDOS spectrum of $\text{[Ru(bpy)$_3$]}^{2+}$ (hydrogen excluded). (a) represents the calculation of $\text{[Ru(bpy)$_3$]}^{2+}$, iodide and water, (b) of $\text{[Ru(bpy)$_3$]}^{2+}$ and water and (c) of gas-phase $\text{[Ru(bpy)$_3$]}^{2+}$. The Ru 4$d$ peaks in (a) and (b) are aligned with the gas-phase 4$d$ peak.

Figure 30: MO comprising atomic orbitals on $\text{[Ru(bpy)$_3$]}^{2+}$ and $\text{I}^{-}$.

however, quickly brought me to the insight that the computational cost increases very rapidly with the number of water molecules included. Periodic boundary conditions would undoubtedly be a better alternative.
7 Final remarks

Improvement of the solar cell requires a detailed understanding of the reaction mechanisms as well as of the interfacial structure. By optimizing the materials, more stable and effective cells can be developed.

It is known that the iodide/triiodide redox couple works exceedingly well for regeneration of the oxidized dye in the dye-sensitized solar cells. In this work, molecular dynamics simulations of iodide and the prototype dye in water solution showed that the iodide ions are likely to be found close to the dye molecule. When the dye, subsequent to photoexcitation, injects an electron into the semiconductor, the iodide ion will thus be favorably positioned in order to give an electron to the dye molecule.

The different steps in the mechanism for the regeneration of the dye is still a topic for further investigation. The next approach would be quantum chemical studies of the oxidized dye and iodide, in combination with molecular dynamics simulations.

Moreover, the electronic structure of iodide and triiodide at the 3\textit{d} and 4\textit{d} levels and at the 5\textit{sp} valence level were calculated with quantum chemical methods and an assignment of the spectra was made. The computed spectra could help to explain the features of experimental photoelectron spectra.

Due to the difference in charge distribution at the terminal and center sites of the triiodide molecule, the core levels split into two lines. The calculated terminal/center splitting agrees well with the experimentally determined splitting. Since the potential felt by an electron in a \textit{d} orbital depends on the orientation of the orbital with respect to the internuclear axis, each of these levels in turn splits into three. The effect is more apparent for the central iodine, leading to a larger broadening of the peak corresponding to photoemission from the central site. In the calculated terminal levels, a very small splitting due to orbital overlap appeared. This fine structure could be expected to be observed in high-resolution photoelectron spectroscopy measurements.

The calculations also showed that relativistic effects are important to take into account for the heavy iodine atom. Bond lengths obtained in relativistic calculations were shorter and the terminal/center splitting larger than in the nonrelativistic case. The value of the spin-orbit coupling, calculated for 4\textit{d} was close to the experimental value.

In the experiments, liquid samples were measured. The theoretical spectra were however computed for single molecules and solvation effects still remain to investigate. The energies should also be more accurately determined by treating the electron correlation thoroughly with perturbation theory.

Another question is how to calculate the intensities of the theoretical spectra. So far, all states have been assumed to contribute to the intensity with equal weight. In the experimental spectra, the intensity is determined by the cross section of interaction between the incoming photon and the atoms in the material. This is a source of differences between computed and measured spectra in the present situation.

The theoretical spectra in this work are limited to simply include emission of a photoelectron from the levels occupied in the ground state; no other effects have been allowed. By extending the active space, thus allowing excitations to higher molecular levels, photoionization mechanisms – like shake-up effects – could be studied further.

To sum up, computational methods prove to be a most useful tool for explaining experimental results. The results presented in this thesis add one piece to the understanding of the processes in the dye-sensitized solar cells. An idea of how to improve the theoretical results is furthermore given, which is perhaps even more interesting and promising for the future.
8 Acknowledgements

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