ELECTRONIC STRUCTURE STUDIES OF RUTHENIUM-BASED CATALYSTS FOR OLEFIN METATHESIS: AN X-RAY ABSORPTION SPECTROSCOPY PERSPECTIVE

by

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ABSTRACT

Interest in olefin metathesis has increased over the years with the development of ruthenium-based catalysts. Their unique properties have allowed their use in numerous industrial and laboratory processes in relatively mild conditions and in combination with a wide range of solvents. Several studies have provided insights into how these catalysts work, but very little has been done in order to understand why they work that way; an important aspect that has the potential of benefiting chemists while designing new catalysts. The research introduced here has focused on the fundamental understanding of their reactivity by exploring their electronic structure, using a combination of synchrotron-based X-ray-absorption (XAS) techniques in combination with DFT calculations and multiplet simulations. As part of the experimental work, samples from various ruthenium-based catalysts classified as first-generation (whenever the ancillary ligand is a phosphine) or as second-generation analogues (whenever this ligand is an N-heterocyclic carbene, NHC) were used. The Ru K-edge XAS data have revealed that the ruthenium centre in second-generation analogues is more positively charged than the corresponding first-generation counterparts. This offers a rationale for previously observed kinetic results, which have shown a slower initial step for the second-generation Grubbs catalyst. At the same time, they raise questions in a more fundamental level on whether or not NHCs are truly better charge donors than phosphine ligands. DFT results are consistent and the ongoing analyses of the Cl K- and C K-edge XAS data indicate similar overall bonding structures between first- and second- generation analogues. In addition, from preliminary results on these edges, two possible identities of substantially different nature have emerged for the LUMO orbital. In this regard, the final conclusion should provide important insights on through which orbital the metathesis reaction gets started. As a side product, the analyses of the challenging Cl K-edge XAS data have inspired the development of a new methodology and a Matlab-based computer program for fitting. Ultimately, the methods and techniques detailed here can serve as the foundation for the comprehensive study of other related systems relevant to olefin metathesis, or in general, to the field of homogeneous catalysis.
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<tbody>
<tr>
<td>ADF</td>
<td>Amsterdam Density Functional (Software Package)</td>
</tr>
<tr>
<td>BP86</td>
<td>Becke and Perdew exchange correlation functional</td>
</tr>
<tr>
<td>CEM</td>
<td>Channel Electron Multiplier</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>ECP</td>
<td>Effective Core Potential</td>
</tr>
<tr>
<td>EDA</td>
<td>Energy Decomposition Analysis</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absoprtion Fine Structure</td>
</tr>
<tr>
<td>GTO</td>
<td>Gauss-type Orbital</td>
</tr>
<tr>
<td>GUI</td>
<td>Graphical User Interface</td>
</tr>
<tr>
<td>HWHM</td>
<td>Half the Width at Half the Maximum</td>
</tr>
<tr>
<td>LF</td>
<td>Ligand Field</td>
</tr>
<tr>
<td>LLCT</td>
<td>Ligand to Ligand Charge Transfer</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand to Metal Charge Transfer</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal to Ligand Charge Transfer</td>
</tr>
<tr>
<td>MPA</td>
<td>Mulliken Population Analysis</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>NHC</td>
<td>N-Heterocyclic Carbene</td>
</tr>
<tr>
<td>NLLS</td>
<td>Non-Linear Least Squares</td>
</tr>
<tr>
<td>RMSE</td>
<td>Root of Mean Square Error</td>
</tr>
<tr>
<td>SCF</td>
<td>Self Consistent Field</td>
</tr>
<tr>
<td>ΔSCF</td>
<td>Slater Energy Corrections in a TD-DFT calculation</td>
</tr>
<tr>
<td>SGM</td>
<td>Spherical Grating Monochromator</td>
</tr>
<tr>
<td>SSE</td>
<td>Sum of Squared Errors</td>
</tr>
<tr>
<td>SSR</td>
<td>Sum of squared differences between the fit and the fit of the response data</td>
</tr>
<tr>
<td>SSRL</td>
<td>Stanford Synchrotron Radiation Lightsource</td>
</tr>
<tr>
<td>SST</td>
<td>Sum of squared differences between the response data and the mean of the response data</td>
</tr>
<tr>
<td>STO</td>
<td>Slater-type Orbital</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>Time-dependent DFT</td>
</tr>
<tr>
<td>TZ2P</td>
<td>Triple Zeta double Polarised basis set</td>
</tr>
<tr>
<td>TZP</td>
<td>Triple Zeta with Polarisation basis set</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-Visible Absorption Spectroscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high Vacuum</td>
</tr>
<tr>
<td>VBCI</td>
<td>Valence Bond Configuration Interaction model</td>
</tr>
<tr>
<td>VNW</td>
<td>Vosko-Nusair-Wilk exchange-correlation functional</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near-Edge Spectroscopy (another name for XAS)</td>
</tr>
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<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
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I never met my grandfather, but if he was alive today, as a former chemist, he would probably be very happy to know that one of his grandsons made it to grad school and wrote a thesis on a topic related to chemistry. Provided there is a "chemistry" gene, I would certainly owe him for my interest in this discipline.

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CHAPTER 1: INTRODUCTION

1.1. GENERAL SCOPE

This Thesis summarises the accumulated efforts to better understand ruthenium-based carbene catalysts and their observed reactivity in the olefin metathesis reaction. Several X-ray absorption spectroscopy (XAS) based techniques and theoretical methods have been used, new methodologies have been developed, and Matlab-based software has been implemented for the analysis of XAS data. These novel methodologies are relevant to our studies and can be applied to similar problems, not only in XAS, but also in other scientific areas for which fitting procedures are important.

The current chapter introduces the olefin metathesis reaction, as well as the historical development of robust, well-established catalysts relevant to this reaction. Of particular interest, in Section 1.3, the ruthenium-based catalysts are introduced along with important contributions towards the understanding of their reaction mechanism; important elusive information related to these compounds is also discussed. In section 1.4, our general strategy to study the electronic structure of such compounds is introduced.

Chart 1.1 depicts the ruthenium-based complexes that are relevant to this thesis work. Primary XAS investigations focused on Grubbs’ first- and second-generation precatalysts (1a & 1b) as well as Piers’ first- and second-generation catalysts (2a & 2b). Complementarily, XAS experiments and theoretical calculations also included the third-generation Grubbs catalysts (4-7), Heppert's carbide complexes (3a & 3b) and Fogg's catalyst 8 (1-3).

Chapter 2 provides a more extensive and comprehensive introduction to the XAS techniques used. The significance of spectral features typical in each of these techniques is explained in detail (Sections 2.3, 2.4 and 2.5). Section 2.6 provides the details on the experimental set-up for relevant XAS experiments. The data analysis procedures involved in the calibration, background subtraction, fitting and normalisation of raw XAS data are introduced in the last section of Chapter 2 (Section 2.7). Chapter 3 is dedicated to the implementation of new methodology for the fitting of complex
spectra in a Matlab-based software package named *Blueprint XAS*. The computational methods used as an aid in the analysis of XAS are introduced in Chapter 4. The results and implications of this work are discussed in Chapters 5 and 6. Finally, in Chapter 7, the conclusions of my work and some recommendations for future efforts in this research area are presented.

**Chart 1.1**  Ruthenium-based complexes relevant to this thesis work.

\[ \text{Chart 1.1} \quad \text{Ruthenium-based complexes relevant to this thesis work.} \]
1.2. THE OLEFIN METATHESIS REACTION

The olefin metathesis reaction is one with no apparent precedent in nature. It involves the recombination of the groups attached to carbon-carbon double bonds as shown in Scheme 1.1. The reaction is accomplished by the use of metal catalysts, the first of which was synthesised and well-defined for this purpose by Richard R. Schrock and co-workers in 1980 (4, 5).

Scheme 1.1 The olefin metathesis reaction. (Products are obtained with non-defined stereochemistry).

\[
\begin{align*}
R_1 & + R_1 & \rightarrow & & R_2 + R_2 \\
R_2 & + R_2 & \\
\end{align*}
\]

The overwhelming number of applications of this reaction nowadays is truly remarkable, especially considering the short time since it was first observed. A large number of olefin metathesis applications in several industries have been growing over the years (see, for example, references (6-24)). The synthesis of numerous complex organic molecules and materials, such as pharmaceuticals, polymers, agrochemicals and natural products, has been facilitated by well-defined catalysts. The importance of the reaction was highlighted by the awarding of the 2005 Nobel Prize in Chemistry to Richard R. Schrock, Robert H. Grubbs, and Yves Chauvin for their pioneering work in the area.

Despite the wealth of accumulated research, there has been an ever increasing academic interest in this area over the years. Most current efforts focus on finding new applications (6, 21, 25, 26), answering some elusive questions regarding the mechanism (27-31), and improving catalysts through systematic tuning of their properties (32-43).

1.2.1. Historical antecedents

The development of olefin metathesis as a catalytic process followed from the observation of several industrial processes involving the polymerisation of ethylene. Starting in the late 1950s, several patents reported novel polymerisation processes
involving cyclic olefins and molybdenum and tungsten compounds, for which their mechanisms of action were not understood. Around the same time, there were also reports about the "disproportionation" of acyclic olefins.

The term "olefin metathesis" was coined by Nissim Calderon (44), who reported several examples of polymerisation of cyclic olefins (45, 46) and suggested that this reaction and the disproportionation of acyclic olefins, reported by others (47), belonged to the same kind of reaction.

There were several early attempts by a number of researchers to understand how this reaction takes place mechanistically (48-51), including also the work of Calderon (50, 51) and Grubbs (52). In 1971, Chauvin published his proposal for the mechanism (53) that is considered to be, to this date, the correct mechanism for the catalysed olefin-metathesis reaction. The active species is a metal alkylidene (also referred to here as a metal carbene) that, upon interaction with the olefin, leads to the formation of an olefin-bound species. This intermediate, then, leads to the formation of a metallacyclobutane species that, after recombination, leads to a different olefin-bound species (Scheme 1.2). Important contributions mainly by Katz (54, 55) and Grubbs (56, 57) helped to further support the understanding of this mechanism.

**Scheme 1.2** Chauvin's generally accepted mechanism illustrating productive cross olefin metathesis.

Synthesis of the first isolated metal alkylidene was accomplished in 1964 by Ernst Otto Fischer (58) and co-workers (I; Chart 1.2). This compound did not exhibit any reactivity towards olefin metathesis, but opened the door for the synthetic development of other active compounds. Fischer's compound (I) consisted of a low oxidation state tungsten metallic centre surrounded by five carbonyl ligands and a singlet carbene. The presence of donor groups, such as the methoxy group (MeO) in compound I, allows for
the existence of an empty acceptor \( \pi \) orbital in the carbon atom (\( \text{CA}_\pi \); Figure 1.1) directly interacting with the metal centre (\( M \)). This acceptor \( \pi \) orbital is formally an antibonding orbital that emerges from the interaction of a \( p \) orbital in this carbon atom with other orbitals in the donor group. The interaction in the double bond between a filled \( d \) orbital in the metal centre (\( M \)) and this empty \( p \) orbital of the carbon atom (\( \text{CA}_\pi \)) is, thus, formally a \( \pi \) back-bonding interaction. Compounds possessing similar electronic structures (such as the Grubbs catalysts) are also classified as \textit{Fischer-type carbenes}.

**Chart 1.2**  Evolution of the metal carbene as an olefin metathesis catalyst.

Another class of metal carbenes, involving a triplet state in the carbon atom of the carbene and early transition metals in high oxidation states, was developed by Schrock and co-workers. In this class of compounds, no donor group is directly attached to the
carbon atom. Hence, no interaction helps to stabilise any of the 2p orbitals in the carbon atom and, as a result, this partially filled orbital ($C_{D\pi}$, Figure 1.1) is more of a donor orbital upon the interaction with the metal centre. Both the $\sigma$ and the $\pi$ interactions in the M-C bonds of a Schrock-type carbene are more covalent in nature (due to the contribution of one electron per atom when forming each bond), the electron density is more localised on the carbene (Figure 1.1) and the reactivity is more like that of a nucleophile.

**Figure 1.1** Molecular Orbital diagram comparing the $\pi$ system in Fischer and Schrock carbenes.
Early attempts by Schrock and co-workers yielded metal alkylidenes that were unable to perform the olefin metathesis reaction (59, 60). The first well-defined carbene ever to catalyze the metathesis reaction involved thallium, and it was synthesized in 1980 (4, 5). This compound was able to catalyze the olefin metathesis of cis-2-pentene. Further refinements yielded the development of a whole new family of Schrock catalysts with the general formula M(=CHR$_1$(=N-Ar)(OR$_2$)$_2$, where M is either molybdenum or tungsten and R$_1$, R$_2$ and Ar are bulky groups (61-64). This family of nucleophilic complexes are among the most active olefin metathesis catalysts known today (II and III, Chart 1.2). Unfortunately, this reactivity is not that specific and these catalysts also show poor stability in air and low tolerance towards other functional groups.

1.3. RUTHENIUM-CARBENE CATALysts FOR OLEFIN METATHESIS

In 1965, Giulio Natta reported ring-opening polymerisation of cyclobutane by using ruthenium trichloride (65). Later efforts by Grubbs showed that the polymerisation of olefins was even possible in the presence of water (66). These observations led to the development of a novel family of ruthenium-based carbene complexes, the first of which was reported in 1992 (67) (IV, Chart 1.2). Further refinements that involved the substitution of phenyl groups in the phosphine ligand of IV, by cyclohexyl (R=Cy) groups, led to the synthesis of a catalyst that was able to perform ring-opening polymerisation reactions in the presence of water and also showed reactivity towards other metathesis reactions involving acyclic olefins (68-70). Compound IV is a Fischer-type carbene (Figure 1.1) and, unlike Schrock complexes, it is electrophilic and highly tolerant to a wide range of protic solvents.

Shortly thereafter, a more robust and easily synthesised catalyst (1a, Chart 1.1), widely known as the first-generation Grubbs catalyst, was developed (71-73). This new compound exhibited remarkable stability in air, and as compound IV, it was highly tolerant to a wide range of solvents and functional groups commonly used or encountered in organic synthesis. Due to this combination of properties as well as its commercial availability, compound 1a is still the most widely used catalyst to perform olefin metathesis in organic synthesis.
Other more challenging synthetic approaches, which are often required in ring-closing reactions, increased the need for more regio-specific catalysts. Kinetic and mechanistic studies (74-76), conducted by the Grubbs group, showed that 1a needed the dissociation of one of its phosphine ligands in order to generate the putative four-coordinate, catalytically active species (A, Scheme 1.3) required to enter the catalytic cycle. Therefore, the obvious strategic move was to develop a catalyst (formally a pre-catalyst in the case of 1, and 4-8)† with an improved phosphine dissociation rate towards the formation of catalyst A.

Scheme 1.3 Olefin metathesis mechanism for ruthenium-based catalysts.

The synthetic development of N-heterocyclic carbenes (e.g., IMes and H2IMes in Chart 1.1) has led (as further explained in Chapter 5) to what have been considered better sigma donors than phosphine ligands. The substitution of one phosphine group by H2IMes in compound 1a led to the formation of 1b (77-86). It was believed that this modification would increase the rate of the initial phosphine dissociation step. However, kinetic studies have demonstrated that the rate constant for this initial step is about two orders of magnitude smaller for 1b than for 1a (75, 76, 87).

† In the rest of this thesis, the word "catalyst" is used to refer to compounds 1 and 4-8.
Regardless of a slower initiation step, compound 1b, widely known as the second-generation Grubbs catalyst, is more active and very effective in ring-closing metathesis reactions. It is also more stable upon heating than 1a, but somewhat more sensitive to air (88).

In addition to the kinetic studies by Grubbs, Chen and co-workers have used a combined quantum mechanical/molecular mechanics (QM/MM) approach to find the transition state energies for several species in different plausible paths (89, 90). These calculations, together with some experiments in gas phase, have supported Grubbs’ proposed mechanism as the most favourable path. They have also shown that the actual catalyst (A, Scheme 1.3) formed from the first-generation pre-catalyst 1a, has a higher barrier towards the formation of the olefin-bound species (B, Scheme 1.3), imposed, in part, by the necessity of rotation around the main axis of the three-fold symmetric phosphine ligand. In contrast, the catalyst species (A) formed from 1b exhibits a lower energy barrier towards the formation of B due to the lack of this three-fold rotation in the N-heterocyclic carbene ligand. These results thus support the kinetic studies by the Grubbs group and provides an underlying foundation (by means of steric) for the observed differences on the overall activity of 1a and 1b, particularly that of the corresponding active species (A).

These combined results by Grubbs and Chen support a rate-limiting step for 1a occurring within the catalytic cycle (once the formation of A has been achieved). By contrast, they suggest that the limiting step when using 1b occurs during the initial phosphine dissociation step (before the formation of A). Chen has termed pre-catalysts like 1a as low-commitment catalysts and those like 1b as high-commitment (90) catalysts (Figure 1.2).

Even though Chen’s research provided insights towards the understanding of the difference in reactivity of 1a and 1b, his work concentrated mainly on certain aspects regarding steric on the active species (A). An explanation for the source of a faster initiation step in 1a than in 1b remained elusive. Also, at a more fundamental level, a more in-depth revision of the conventionally accepted electronic properties of N-heterocyclic carbene ligands versus the electronic properties of phosphine ligands was
also necessary to understand the source of the apparent discrepancy in the difference of the rate in the initial dissociation step.

Figure 1.2 Low-commitment (1a) versus high-commitment (1b) catalysts towards the olefin metathesis reaction.

The need in 1a and 1b for an initial dissociation step before the formation of the active catalytic species (A) motivated the synthesis of new compounds for which olefin metathesis can be accomplished with a faster initiation step (or even without it). Hoveyda (91), who substituted the phosphine ligand in compound 1b by a carbene-ether moiety (V, Chart 1.2), achieved an improvement in the overall activity of the second generation-type catalyst. The underlying idea behind the development of V was to incorporate the leaving group of the initial dissociation step to the backbone of the carbene. In a similar approach, Grubbs and co-workers substituted the phosphine ligand in compounds 1a or 1b, with a pair of more labile pyridine ligands (92). The resulting synthesised compounds (4 and 5, Chart 1.1), collectively known as the third-generation Grubbs catalysts, exhibited an extremely fast initiation step (93). Overall, a higher activity was observed for the 3-bromopyridine complexes likely due to the
withdrawing properties of bromine, which helps to slow down the association step when going from catalyst A to the original pre-catalyst (5a or 5b) (93). A drawback for these complexes, however, is that their reactivity seems to be less specific, and so they are more sensitive to heat, air and humidity than complexes 1a and 1b (94).

In other recent developments, Piers and co-workers have accomplished, with the synthesis of catalysts 2a and 2b (termed here as first- and second-generation Piers catalysts, Chart 1.1), the near-elimination of the initial step, overall (95, 96). Compounds 2a and 2b exhibited faster initiation rates and higher conversions than even Schrock carbenes (95). Compared to Grubbs’ pre-catalysts, these two four-coordinated ruthenium complexes are the closest stable analogues to the active catalysts (A) with one important structural difference: the \( \pi \) system in Piers complexes is rotated by 90 degrees with respect to the \( \pi \) system in 1a and 1b. Furthermore, since these two complexes possess a phosphonium group attached to the backbone of the catalysts, they are formally cationic and are accompanied in their solid form by an inert large anionic group. By means of synthesizing 2b with four different anions (BF\(_4^–\), B(C\(_6\)F\(_5\))\(_4^–\), CF\(_3\)CO\(_2^–\) and B(C\(_6\)H\(_5\))\(_4^–\)), it has been demonstrated that these anions do not significantly modify the structure of the cation, nor do they interfere substantially with the cation activity towards the ring-closing metathesis reaction (96).

Despite all of the advances during the last two decades, there are still unresolved issues related to the mechanism and the structure of the catalysts and the intermediates involved. In recent investigations, there is no consensus, for example, on whether the association of the olefin to the active catalyst A occurs via the formation of B with the two chlorine ligands in trans or with these two ligands in cis (or perhaps both, depending on the structure of the olefin). No conclusive answer on this has been given either experimentally (27, 28, 97, 98) or suggested by theoretical calculations (29, 99). The implications of the understanding of this particular issue is important, since the structure of the other intermediate, the metallacyclobutane (C), depends on this and so does the stereochemistry of the final product.

Another question that remains elusive is the role of the chlorine ligands in the overall activity of these catalysts. Perhaps there is a specific balance between lability
and stability that accounts for either a cis or trans olefin-bound intermediate (B) that can be tuned (by the use of other anionic ligands with specific properties) to favour one way or the other. Notably, part of Fogg’s research has focused on the development of catalysts that make use of other anionic ligands, or a combination of them, resulting in catalysts with high activities towards some specific olefin metathesis reactions (100-103).

The need for a more fundamental understanding of the mechanism and the structure and reactivity of these catalysts is evident and essential for a more rational catalyst design and development. The main goal of this thesis work was to develop a useful methodology for electronic-structure investigations on these compounds by the use of X-ray absorption spectroscopy (XAS) as the primary experimental technique, in conjunction with Density Functional Theory (DFT) calculations and multiplet simulations.

1.4. STRATEGY

Figure 1.3 illustrates the underlying strategy, indicating the steps in the analyses involved to complete this thesis work. Since XAS is an element-specific technique (see Chapter 2), several XAS experiments were explored to map out the electronic structure of ruthenium-carbene catalysts from different perspectives: transition metal K-edge XAS, to investigate the relative effective nuclear charge in the ruthenium centre; ligand K-edge XAS, to estimate Ru-Cl bond covalencies (Cl K-edge XAS) and to explore Ru-C bonding (C K-edges XAS); and Metal L-edge XAS (Ru L2,3-edges XAS) to investigate ligand-field and differential orbital covalency interactions around the metal. The details on these techniques are given in Chapter 2.

To undergo the XAS experiments described in this thesis, complexes 1a and 1b were purchased from sigma Aldrich and used as received. Moreover, Compounds 2-3 were synthesized by Warren Pier's group (95, 104), whereas compound 8 was prepared by Deryn Fogg's group, as described elsewhere (100). Finally, bispyridine complexes 4-7 were all synthesized in the Kennepohl group by my co-worker, Kendra Getty (3).
Before XAS experiments, NMR was used to check the purity of all complexes. Storage, manipulation and transportation of all of the samples before and during the XAS experiments were all carried out under an inert nitrogen (N₂) atmosphere. The experimental set-up details for each of the XAS experiments are given in Section 2.6.

The interpretation of XAS spectra required not only traditional and novel methodologies for fitting, but also a combination of theoretical approaches to obtain as much information as possible. DFT methods (Sections 4.1 and 4.2) were the primary theoretical tools applied. In order to explore electronic relaxation effects and to evaluate differential orbital covalency, a novel approach to undergo multiplet simulations is
implemented in a new Matlab-based program under development (see sections 2.3, 2.4, 4.3, 6.1.4 and Chapter 7 for details).
CHAPTER 2: X-RAY ABSORPTION SPECTROSCOPY (XAS)

2.1. SYNCHROTRON RADIATION SOURCES

Before the 1970s, particle accelerators were facilities exclusively used for experiments on high-energy particle physics; the emitted radiation from such facilities was considered a byproduct (105). The success of the few experiments performed parasitically using this radiation led to the eventual development of synchrotron facilities dedicated exclusively to the production of light, and the use of such in specific experiments. One of the new experimental techniques that emerged from synchrotron radiation sources was X-ray absorption spectroscopy (XAS). Previously, other experimental techniques were in use (e.g., X-ray diffraction and photoelectron spectroscopy), but the experiments available were severely restricted due to the narrow number of discrete X-ray lines with good intensity that were available from other sources.

A synchrotron facility generally consists of a storage ring ranging from 50 m to 1.5 km in circumference, as well as an injection system, which typically includes a booster ring and a linear accelerator or linac (106) (Figure 2.1).

The storage ring is an arrangement of magnets and other components that allows a beam of electrons (or positrons) to travel under ultra-high vacuum conditions (≤10⁻⁹ mmHg) to nearly the speed of light in a closed loop for several hours (106, 107). The magnets are the main components directly controlling the path of the electrons and are primarily responsible for the radiation that is produced. Some of this radiation leaves the ring through tangentially located beamlines located all along the ring (Figure 2.2).

In early first-generation facilities, the bending magnets (b_m, Figure 2.2) and the quadrupole magnets (Q_m, Figure 2.2) were the only kind of magnets in storage rings. However, in the early 1980s, other magnetic devices, commonly known as insertion devices (ID, Figure 2.2), were developed and later located in the straight sections of storage rings with the purpose of optimising the brilliance of the produced radiation and increasing the flux of high energy photons (105).
Prior to their injection into the storage ring, electrons are accelerated first in a linac and then in a booster ring to reach energies several orders of magnitude superior to the electron's rest mass energy \( m_c^2 = 0.511 \text{ MeV} \). (This energy corresponds to 3 GeV in the case of the Stanford Synchrotron Radiation Lightsource, SSRL, where the experiments relevant to this thesis work were conducted.) Once in the storage ring, the energy lost through radiation, is reloaded in a special cavity chamber located in one of the straight sections of the ring, where electromagnetic fields at radio frequencies (rf) are maintained. Even at extremely low pressures, collisions of some of the electrons in the beam with residual air molecules are inevitable. This leads to an approximately exponential decay of the intensity of the electron beam. Consequently, the electron beam gets replenished after several hours of operation (every eight hours in the case of SSRL) by the injection of a new pre-accelerated electron beam.

2.1.1. Radiation patterns effected by magnets

At 3 GeV, the bending magnets, located in the curved sections of the storage ring, deflect the beam of electrons, forming a radiation cone pattern with an opening angle of
$mc^2/E = \gamma^{-1}$ radians (106) (Figure 2.3). A wider range of brighter photons is achieved by the use of *wiggler* magnets, which are insertion devices located in the straight-line sections of the storage ring (Figure 2.2).

**Figure 2.2** (a) A typical storage ring; (b) Close-up detail showing the storage ring components; (c) A Wiggler magnet affecting the electron trajectory.

A wiggler magnet consists of an array of alternating polarity magnetic poles that bends the beam of electrons at a much larger angle compared to $\gamma^{-1}$. This device is designed in such a way that no net bending of the trajectory of the electrons occurs. The incoherent superposition of the radiation produced by each individual bend gives rise to a net radiation cone pattern with an opening angle at least one order of
magnitude broader than in the case of the radiation produced by bending magnets (Figure 2.3b).

Another insertion device commonly used is the so-called undulator magnet. The configuration of undulator magnets is very similar to that of wigglers. However, the shorter alternating $N$ magnetic poles cause smaller bending angles in the electron trajectory comparable to $\gamma^{-1}$ and thus, the intrinsic brightness of the synchrotron radiation is preserved and the interference of essentially collinear source points enhance the brightness of only certain wavelengths. Consequently, rather than generating a continuous-like radiation profile, the radiation produced with an undulator magnet is a somewhat discrete profile of very bright spectrum lines with a radiation cone pattern possessing an opening angle of only $\left(\gamma \sqrt{N}\right)^{-1}$ radians (Figure 2.3c).

The perturbing action of bending magnets and insertion devices cause the expansion of the transverse section of the beam of electrons in the storage ring. Therefore, the use of quadrupolar magnets is required to refocus the beam to ensure small transverse dimensions. Other focusing magnets (sextupoles, steering magnets) also provide corrections that allow large storage intensities and that help to maintain the electron trajectory orbit so that the radiation source points do not move.

2.1.2. Other synchrotron components

Synchrotron sources are incredibly complex facilities in which all of their individual diverse components need to work synchronously to obtain good quality data. In addition to the family of magnets briefly described in the previous section, other important components include powerful vacuum turbo pumps that maintain space-like vacuum conditions, as well as beamline components such as detection instruments and other electronic and optical devices, such as focusing and collimating mirrors, slits and at the core of a beamline, a monochromator.
Figure 2.3  Radiation cone patterns effected by (a) Bending magnets, (b) Wiggler magnets and (c) Undulator magnets (106).
Monochromators are optical devices that filter a section of the beam into a specific wavelength with a narrow bandwidth. The monochromatizing element in this device, which typically works on a reflection mode, is either a crystal, for high energy (or hard) X-rays, or an artificial grating, commonly with a pitch of 600 lines/mm or 1,000 lines/mm, for low energy (or soft) X-rays. The space period between lattice planes (on a crystal monochromator), or adjacent lines on gratings, defined here as $d$, determines the diffraction properties of the device, as given by Equation 2.1. From this equation, it is clear that the $d$-spacing should be significantly smaller for the case of hard X-rays, which justifies the use of crystals.

**Equation 2.1** Diffraction conditions in crystal and grating monochromators (108).

$$d(\sin \theta_i + \sin \theta_d) = n\lambda$$

*Where,*

$d =$ spacing between lines or lattice planes

$\theta_i =$ incidence angle

$\theta_d =$ diffraction angle

$\lambda =$ X-ray wavelength

$n =$ diffraction order

Figure 2.4 illustrates a double crystal monochromator arranged in a (+,-) configuration as is normally used at beamlines 6-2, 4-3 and 7-3 of SSRL (the work stations where most of the data relevant to this thesis were collected). The parallel geometry of the crystals in this configuration keeps a constant direction in the beam, while scanning a wide range of photon energies (108).

Figure 2.5, on the other hand, illustrates a spherical grating monochromator (SGM) mounted in a Rowland-circle geometry, as used in beamline 10-1 of SSRL (where experiments on the C K-edge were performed). The operation of this device
when selecting photon energies is based on the motion of the grating with respect to fixed entrance and exit slits.

**Figure 2.4** Parallel configuration in a double crystal monochromator

![Figure 2.4](image)

**Figure 2.5** (a) Side and (b) Top view of a spherical grating monochromator (SGM), mounted in a Rowland-circle geometry, where both the entrance slit (source) and the exit slit (Image) are located (105, 108-111).

![Figure 2.5](image)
2.2. GENERAL INFORMATION ON XAS

XAS is, in practical terms, a synchrotron-based technique. It involves the excitation of core electrons into empty molecular orbitals of a given compound as well as the ionisation of these electrons to the continuum of states. The absorption process occurs within a very specific range of energy, depending on the nature of the donor core orbitals (for example, see Table 2.1).

Figure 2.6 shows some of the most common transitions studied in XAS. The plot shown on the left corresponds to the excitation and ionisation of the core 1s electrons of a given element. The typical XAS spectrum consists of a pre-edge structure, which may include several peaks, as a result of the transitions from the donor core electron into the several low-lying empty molecular orbitals; and of an edge jump, which appears slightly higher in energy than the pre-edge features and that corresponds to the ionisation of the core electron.

As indicated in Figure 2.6, specific labels are used to identify the kind of transitions studied on XAS. The capital letter in this label indicates the shell from which the donor electron has been excited (K for $n=1$, L for $n=2$, M for $n=3$, and so on). Whenever necessary ($n>1$), the subscripted number indicates the kind of donor orbital involved in such transition (e.g., L$_1$ refers to a transition originated from a 2s core electron, L$_2$ and L$_3$ to transitions originated from a 2p core electron, and so on). Importantly, when generating a core hole in $mp$ or $nd$ levels, spin-orbit coupling of these core electrons splits the possible transitions into two edges (see Section 2.5 for further details on this). Table 2.1 lists the corresponding energies, relevant to this thesis work, at which the corresponding ionisation occurs for the natural forms of ruthenium, chlorine, phosphorous and carbon (112).

In XAS, the edge jump position provides valuable information about the oxidation state of the donor atom. Conventionally, the inflection point of the edge jump is taken as the energy value used for correlation with the oxidation state. In general, a shift in the inflection point of an edge jump of about ~2 eV corresponds to a change in the oxidation state of the source element, by one unit (113). Therefore, XAS is extremely sensitive to changes in the electronic environment. Additionally, the position and
The oscillatory structure observed at energies above the energy of the edge jump is often referred to as the extended X-ray absorption fine structure (EXAFS). These oscillations result from the constructive and destructive interference of the photoelectrons due to back-scattering from other nuclei near the source atom. The resulting EXAFS structure is often analysed by researchers, in a wide range of disciplines, with the purpose of finding the geometry around the source atom in a given compound or material, particularly in the cases in which the process of growing a crystal has proven to be difficult. Especially sensitive to the surrounding environment are the donor electrons in the K-Shell. Therefore and not surprisingly, researchers interested in finding geometrical information often collect data within the K-edge region of interest. The analysis of the EXAFS region is not relevant to this thesis work and therefore no further details are given in the next sections. However, the interested reader can consult other sources of information on the topic (114).
Figure 2.6 Left: A typical K-edge XAS spectrum; Right: Tags used to label common transitions in XAS.

2.2.1. Electric dipole selection rules and XAS

Upon the interaction of radiation with matter, the probability for an absorption process can be expressed in terms of Fermi’s golden rule (115), (Equation 2.2). According to this expression, an absorption process is optimal when the energy of the
incident photons ($h\nu$) is in resonance with the difference of energy between the ground and excited states (E’-E).

Equation 2.2  Fermi’s golden rule and the interaction of radiation with matter (115, 116).

\[
W_{J,J'} = \frac{4\pi^2}{\hbar} |U_{J,J'}(k)|^2 \delta(E' - E - \hbar
\nu)
\]

\[
= \frac{4\pi^2}{\hbar} \times \frac{e^2 A_0^2}{4m^2c^2} \times |\langle JM | e^{ik\cdot r} \epsilon \cdot p | J'M' \rangle|^2 \delta(E' - E - \hbar \nu)
\]

Where,

- $W_{J,J'} = \text{Transition probability per unit of time}$
- $\hbar = \text{Planck's constant}$
- $e = \text{Electron's charge}$
- $m = \text{Electron's mass}$
- $c = \text{Speed of light}$
- $A_0 = \text{Vector Potential amplitude}$
- $k = \text{Light propagation vector}$
- $\epsilon = \text{Electric field polarization vector}$
- $r = \text{Electron position operator}$
- $p = \text{Electron momentum operator}$
- $e^{ik\cdot r} = \text{Plane wave}$

\[
e^{ik\cdot r} = 1 + ik \cdot r + \frac{(ik \cdot r)^2}{2!} + ... = \sum_{m=0}^{\infty} \frac{(ik \cdot r)^m}{m!}
\]

- $\delta = \text{Dirac delta function}$
- $\langle JM \rangle = \text{Bra ground state wave function}$
- $| J'M' \rangle = \text{Ket excited state wave function}$

However, energy resonance is not the only important aspect for a transition to have a significant transition probability; conservation of angular momentum is just as
important. In this sense, the angular momentum of the incident photons imposes further restrictions (see below).

The matrix element $U_{jj'}(k)$ in Equation 2.2 directly couple the interaction of the electromagnetic field of radiation with the electric and magnetic moments of the electron being excited. The multipole expansion of the operator in $U_{jj'}(k)$, (involving a Taylor series in $e^{ikr}$) is useful to obtain separate contributions (e.g., dipole, quadrupole, and so on) of the electric and magnetic moments of the transition. The dominant contribution in this expansion is given by the electric dipole (obtained in the approximation $e^{ikr} \sim 1$), (115). The electric dipole is a tensor of rank 1 (see Equation 2.3) and therefore has the equivalent of an angular momentum quantum number of $J_{hv} = 1$.

**Figure 2.7** A plane-polarised electromagnetic wave within the dipole approximation.

Under the dipole approximation, the electric ($\mathbf{E}$) and magnetic field ($\mathbf{B}$) are represented as vectors in a plane-polarised electromagnetic wave in the propagation direction ($\mathbf{k}$), (Figure 2.7). Using this approximation and the Wigner-Eckart theorem (117-119), a useful expression for the total oscillator strength, $f_{jj'}$ (116) is obtained: Equation 2.3 expresses the total oscillator strength in terms of the total angular momentum ($J$) and the corresponding magnetic quantum number (M) of the ground ($|JM\rangle$) and excited states ($|J'M'\rangle$).
The 3-j symbol in Equation 2.3 is non-zero only if the triad \((J1J)\) satisfies the triangle relations, for which, \(\Delta J \equiv J - J' = 0, \pm 1\) and with the restriction that \(J = J' = 0\) is not allowed.

**Equation 2.3**  Total oscillator strength for electric-dipole-allowed transitions (116).

\[
f_{JJ'} = \frac{8\pi^2 m \nu}{3h} \left| \sum_q <JM|P^{(1)}_q|J'M'> \right|^2
\]

\[
= \frac{8\pi^2 m \nu}{3h} \left| \sum_q <J||P^{(1)}||J'> \right|^2 \sum_q \left( \begin{array}{ccc} J & 1 & J' \\ -M & q & M \end{array} \right)^2
\]

\[
= \frac{8\pi^2 m \nu}{3h} S \sum_q \left( \begin{array}{ccc} J & 1 & J' \\ -M & q & M \end{array} \right)^2
\]

\[
= \frac{8\pi^2 m \nu}{3h} (-1)^J [J]^{1/2} [J']^{1/2} \left( \begin{array}{ccc} J & 1 & J' \\ 0 & 0 & 0 \end{array} \right) \sum_q \left( \begin{array}{ccc} J & 1 & J' \\ -M & q & M \end{array} \right)^2
\]

Where,

\(f_{JJ'} = \text{Total oscillator strength}\)

\(m = \text{Electron’s mass}\)

\(h = \text{Planck’s constant}\)

\(\nu = \text{Frequency of incident photon}\)

\(P^{(1)}_q = \text{qth component of the electric dipole moment for } N \text{ electrons}\)

\[= -e \sum_{i=1}^N r_i, q = -1, 0, +1\]

\(S = \text{Electric dipole line strength}\)

\([J] = 2J + 1\)

\([J'] = 2J' + 1\)

Furthermore, it follows from parity restrictions (imposed by the 3-j symbol of the reduced matrix element proportional to \(S\)), that \(J + 1 + J'\) must be even, leading to the
selection rule: \( \Delta J \equiv J - J' = \pm 1 \). In other words, to preserve angular momentum under the electric dipole approximation, the total angular momentum of the excited state must be increased (or decreased) by one unit in relation to the total angular momentum of the ground state.

In summary, transitions with significant transition probability involve states for the ground and excited states whose difference in energy is in resonance with the incident photon and whose angular momentum differs by one (e.g., \( p \leftarrow s \), \( d \leftarrow p \), etc.)

**Figure 2.8** Pre-edge features in a XAS spectrum involve bound transitions to acceptor orbitals with a well defined angular momentum. Therefore, a discrete number of transitions is expected in this region. The edge jump, however, involves ionisation and therefore radial wave functions of free electrons for which any angular momentum is possible. Hence, a continuous number of transitions constitute the edge jump.

In XAS, the donor orbital typically involves a core orbital within a well localised atomic nucleus. The acceptor orbital, which in the case of bound transitions corresponds to an empty molecular orbital, needs to have an important contribution of an atomic orbital within the same nucleus, and must have an angular momentum that differs by one in relation to the donor orbital.
In contrast to bound transitions, the edge itself, as stated in the previous section, originates due to transitions to states in the continuum. However, states in the continuum can possess any value for angular momentum (depending on the kinetic energy (KE) of the free electrons promoted to these states), and therefore the edge jump can be envisaged as a continuous number of transitions to each of these states (Figure 2.8).

The significance of the features near the edge in various types of XAS experiments is explained in more detail in the next three sections of this chapter (2.3-2.5).

2.3. TRANSITION METAL K-EDGE X-RAY NEAR EDGE SPECTROSCOPY

Transition metal X-ray absorption near-edge spectroscopy (XANES) is an experimental technique involving the ionisation of core 1s electrons of a transition metal in a given compound or material. The resulting spectrum is characterised by a very intense edge jump structure attributed to the ionisation process, followed by the extended X-ray fine structure (EXAFS) region, from which geometrical information can be obtained.

Conventionally, the inflection point of the edge jump is taken as the ionisation energy of the 1s electrons in the metal (IE_{M1s}). This quantity is sensitive even to small changes in the local metal charge. Hence, transition metal XANES constitutes an excellent probe for changes in the metal charge due to changes in the ligand environment (120, 121). Since these measurements are relative, the use of references is required (typically the pure metal) (120-122). For the purpose of accurately locating the inflection point of an edge jump, the maximum of the first derivative in the XANES region is used. However, in cases where the pre-edge is large enough and close in energy to the ionisation edge, this maximum gets shifted to higher energies. While studying a series of complexes with similar structure, poor conclusions can result unless this systematic error remains constant (in quality and quantity) in all of the complexes (including the reference). Fortunately, relatively simple fitting procedures, following the methodology discussed in section 2.7, are typically good enough to solve this problem.
Since the low-lying molecular orbitals in the metal are \textit{nd} based, the features in the pre-edge region are due to transition to these orbitals (\textit{nd}←\textit{1s}). These transitions are, in principle, not electric dipole allowed and, as a result, the intensity of the pre-edge is very weak (practically unnoticeable) in centro-symmetric complexes. Substantial intensity in this region is an indication of a broken centro-symmetry, which allows for the mixing of higher \((n+1)p\) orbitals with the \textit{nd} orbitals in the metal (120) (Figure 2.9). The pre-edge feature can therefore provide some important insights related to distortions in the geometry of transition metal complexes.

\textbf{Figure 2.9}  Transition metal K-edge XAS spectrum for an hypothetical centro-symmetric (D\textsubscript{4h}) and an hypothetical non-centrosymmetric complex (D\textsubscript{2d}).

\[ \Psi_E = \sqrt{1 - \alpha^2} \left\{ c_1 |M_{nd}\rangle + c_2 |M_{(n+1)p}\rangle + c_3 |M_{(n+1)s}\rangle \right\} - \alpha |L_{mp}\rangle \]

. Figure 2.9 illustrates the metal K-edge XAS spectrum of two hypothetical complexes with practically the same charge in the metal (same observed ionisation energy of the 1s orbital, IE\textsubscript{M1s}). In one case, the centro-symmetric D\textsubscript{4h} complex exhibits a negligible pre-edge feature. The non centro-symmetric D\textsubscript{2d} complex, on the other
hand, exhibits a pre-edge feature due to substantial mixing of the $nd$ orbitals with the $(n+1)p$ orbitals in the metal.

2.4. LIGAND K-EDGE X-RAY ABSORPTION SPECTROSCOPY

Understanding metal-ligand (M-L) chemical bonds in transition metal complexes is essential to understand their reactivity and physical properties. An important aspect of bonding in these compounds is the amount of covalent mixing or electron delocalisation between the metal and the ligand, referred to here as covalency.

Due to the ever-expanding capacity of computers and their accessibility everywhere, computational methods (particularly DFT methods) are, by far, the most widely used methods to predict covalency as a way to rationalise reactivity. However, experimental methods are crucial to evaluate and calibrate these computations. Several experimental techniques can be applied for this purpose (123, 124). To mention a few; Electron Paramagnetic Resonance (EPR), based on ground state measurements of g-value, metal hyperfine and ligand superhyperfine coupling constants and applied only to non-diamagnetic materials; X-ray photoelectron spectroscopy (XPS), based on excited-state and electronic relaxation effects measurements which are suitable only for solid or gaseous samples; and UV-Vis absorption spectroscopy through the interpretation of ligand-to-metal charge transfer (LMCT) and d-d transition bands. Additionally, X-ray absorption methods have proven useful in the evaluation of covalency, particularly ligand K-edge XAS and Metal L-edge XAS (see next section).

Quantitative ligand K-edge XAS is an experimental technique pioneered by Solomon et al, at Stanford University (125-129). After its successful initial development, this technique has been applied to extract M-Cl and M-S covalencies in numerous studies involving metal chlorides, metalloenzymes and other compounds of chemical and biological relevance (130-134).

2.4.1. Ligand pre-edge intensity and covalency

The ligand K-edge XAS pre-edge involves the transition from $1s$ core electrons of the ligand into the low-lying empty molecular orbitals of the metal complex. In general,
the acceptor orbitals are typically anti-bonding orbitals whose wave function can be described by Equation 2.4.

**Equation 2.4**  Wave function describing low-lying empty molecular orbitals in M-L bonding.

\[
\Psi^* = (1 - \alpha^2)^{1/2}|M_{nd}\rangle - \alpha|L_{mp}\rangle
\]

**Where,**

- \(\Psi^*\) = Low-lying empty MO wave function
- \(|M_{nd}\rangle\) = Transition Metal (d) atomic orbital wave function
- \(|L_{mp}\rangle\) = Ligand (p) atomic orbital wave function
- \(\alpha^2\) = Covalency in terms of ligand contribution

The donor orbital, however, is a very well localised atomic orbital in the ligand. Consequently, and as opposed to LMCT transitions in absorption spectroscopy in which the donor is also a molecular orbital, the transition dipole moment integral (Equation 2.4) in the pre-edge XAS transition is also localised in the ligand (126). In other words, the ligand pre-edge transition in XAS can be imagined as a quasi-ligand LMCT transition (Figure 2.10).

Consequently, the relationship between the intensity of the peak and the covalency of M-L bonds using ligand K-edge XAS can be significantly more straightforward to extract than in LMCT bands. As indicated in Equation 2.5, the intensity of the pre-edge peak is, in principle, directly proportional to the amount of ligand \(mp\) character (\(\alpha^2\)) in the low-lying molecular orbitals (Figure 2.11) (125-128).
Equation 2.5  Relationship between covalency and Intensity of pre-edge transitions in ligand K-edge XAS

\[ I(\Psi^* \leftarrow L_{1s}) = C|\langle L_{1s}|r|\Psi^* \rangle|^2 \]

\[ = C(1 - \alpha^2)|\langle L_{1s}|r|M_{nd} \rangle|^2 + C\alpha^2|\langle L_{1s}|r|L_{mp} \rangle|^2 \]

\[ = \alpha^2 C|\langle L_{1s}|r|L_{mp} \rangle|^2 \]

\[ = \alpha^2 I(L_{mp} \leftarrow L_{1s}) \]

Where,

\[ I(\Psi^* \leftarrow L_{1s}) = \text{Intensity of pre-edge transition} \]

\[ I(L_{mp} \leftarrow L_{1s}) = \text{Intensity of ligand-centered atomic transition} \]

\[ \langle L_{1s}|r|\Psi^* \rangle = \text{Pre-edge transition dipole moment integral} \]

\[ \langle L_{1s}|r|L_{mp} \rangle = \text{Intrinsic Ligand-centered atomic transition dipole moment integral} \]

\[ \langle L_{1s}|r|M_{nd} \rangle \rightarrow 0 \]

\[ C = \text{Proportionality constant} \]

\[ \alpha^2 = \text{Covalency in terms of ligand contribution} \]

As implied by the demonstrative relations given in Figure 2.11, the intensity of a pure, ligand-centered \( mp \leftarrow 1s \) transition is included in the proportionality constant, leading to a new constant \( (C\langle L_{1s}|r|L_{mp} \rangle^2 = 1/k^2) \). This approximation is valid provided the intrinsic dipole moment integral, \( \langle L_{1s}|r|L_{mp} \rangle \), remains unchanged from one compound to another. Under these conditions, the analysis of ligand K-edge XAS data is relatively simple if a reliable reference is available.
Figure 2.10 Comparison between "LMCT" transitions in UV-Vis absorption spectroscopy and ligand K-edge XAS (126).

However, three important factors may complicate the analysis of pre-edges: 1) the effective nuclear charge on the ligand (Z\text{eff}), which has a direct impact on the radial distribution of the wave functions of the ground and excited states; 2) electronic relaxation effects of ligand orbitals, which could give rise to important differences in the metal-ligand bonding, relative to that in the ground state; and 3) multiplet effects that lead to ligand-field electronic states spread over a wider range of energy.

2.4.2. Charge effects on dipole moment integrals

The value of Z\text{eff} is related to the nuclear charge in the ligand as follows: the influence of the nuclear charge (Z) into the electrons is increased (according to Z\text{eff} = Z - \sigma) upon charge donation from the ligand to the metal or other adjacent groups (by reducing the amount of shielding, \sigma). Therefore, the reduction of the negative charge in the ligand has the effect of contracting the size of the ligand orbitals, \text{L}_{1s} and \text{L}_{mp}, and of increasing the value of the intrinsic dipole moment integral, \langle \text{L}_{1s}|r|\text{L}_{mp}\rangle, as a consequence. Additionally, covalent bonding itself influences the value of this integral by putting some \text{mp} electronic density in the region between the metal and the ligand.
The Solomon group at Stanford has reported that the effect of the nuclear charge in the value of this integral (by means of an estimate, using Slater rules and by further Hartree-Fock calculations) is linear and very small in the case of chlorine but somewhat more significant in the case of sulphur, for which a wider range of oxidation states is typical in XAS studies.

The chlorine atoms in the Grubbs catalysts and related compounds (Chart 1.1) relevant to this thesis work have a formal oxidation state of -1. Therefore, and based on the calculations by the Solomon group, it is reasonable to consider that the change in the negative charge of the chlorine atoms, from one compound to another in this series, is not expected to have a significant impact on the value of the dipole moment integral $\langle \text{Cl}_{1s}|\text{r}|\text{Cl}_{3p}\rangle$. Hence, in the analysis of the Cl K-edge XAS data for the ruthenium based catalysts, the corresponding value for this integral in $D_{4h}$-CuCl$_4^{2-}$ was used as a reference and considered as a constant (Chapter 6).
2.4.3. Electronic relaxation effects

XAS is not formally a probe for the electronic structure of the ground state, but instead, a probe for the combined excited and ground states. In principle, as the 1s core hole in the ligand is being created ($C_L$; Figure 2.12), the valence orbitals of the ligand are stabilised due to less shielding from its nuclear charge. Conversely, upon the occupation of a metal $nd$-based orbital due to the pre-edge transition, the repulsion created by the additional electron causes the expansion and destabilisation of the orbitals in the metal. Under these circumstances, if a low-lying empty molecular orbital is close in energy to the acceptor molecular orbitals, the creation of additional pathways for relaxation is possible. This phenomenon, known as electronic relaxation, is thus a manifestation of the changes occurring in the final state upon the creation of a core hole in the ground state (110).

Donor ligands, such as chlorine or sulphur, do not possess themselves a low-lying molecular orbital to assist with electronic relaxation pathways (126). However, in certain complexes, where other adjacent groups in their molecules have a low-lying orbital available, the mixing of the parent excited state with a metal-to-ligand charge transfer (MLCT), a ligand-to-metal charge transfer (LMCT) or a ligand-to-ligand charge transfer (LLCT) state is possible. As a result, instead of observing a single peak transition, a "shake-up" satellite peak emerges from this, making the whole interpretation and analysis of pre-edge features in ligand K-edge XAS somewhat more complicated.

Figure 2.12 illustrates two of the simplest scenarios in ligand K-edge XAS of transition metal complexes. The first one involves ligands possessing low-lying acceptor orbitals, whereas the second considers a situation in which the transition metal complex has only donor ligands (that is the case in metallic chloride complexes, for example). In the case of acceptor ligands, using the valence bond configuration interaction (VBCI) formalism, the "pure-ligand" final state configuration is represented as $C_L:M_d^{n-1}L_A^-$. Originally, in the ground state, this configuration is higher in energy than the pure-metal configuration $M_d^n$, but due to the coulombic interaction of $C_LM_d^{n-1}L_A^-$ with the core hole ($C_L$=1s) in the ligand, $Q(C_L,L_A^-)$, the energy of this could likely move
below the energy of $\text{C}_\text{L} \text{Md}^n$ in the final state. Conversely, in the second scenario, the relative energy of the "pure-ligand" charge-transfer configuration $\text{C}_\text{L} \text{Md}^{n+1} \text{L}_\text{D}$, which already falls below the energy of $\text{Md}^n$ in the ground state, will go further down in energy due to the coulombic interaction with the core hole ($Q(\text{C}_\text{L}, \text{L}_\text{D})$).

**Figure 2.12** Schematic picture for the final state in ligand K-edge XAS of transition metal complexes, in two simple scenarios. Descriptor $\text{C}_\text{L}$ is omitted in "pure" states, for simplicity.

Upon covalent mixing, the "pure" states generate the possible excited states. In the former case, two VBCI excited states described by $\Psi_A$ and $\Psi_B$ are possible. $\Psi_A$ is responsible for a main peak feature (due to its higher ligand character) and $\Psi_B$ is responsible for a satellite, smaller peak feature. In the case of donor ligands, however,
due to the relative occupancy, only the transition to $\Psi_B$ can be accessed. (The essential difference between the occupancy in these two cases is that the state $\text{CuLM}_d^{-1}\text{L}_{A^-}$ possesses a partially filled structure with a single electron in $\text{L}_{A^-}$, whereas $\text{CuLM}_d^{n+1}\text{L}_D$ contains a single hole in $\text{L}_D$).

Electronic relaxation effects are negligible in relatively simple compounds such as metal tetrachlorides or sulphur model complexes. In some ruthenium carbene complexes, however, electronic relaxation has been an important effect that cannot be ignored. The analysis of Cl K-edge XAS data in such cases has been assisted by time-dependent DFT calculations with Slater $\Delta$SCF energy corrections (see Section 4.2.4).

### 2.4.4. Multiplet effects

Ligand K-edge XAS data is often analysed using a single-particle model, in which each observed feature in the spectrum corresponds to the transition to a particular orbital of a group of nearly degenerate orbitals. In some cases, where ligand-field and electronic-relaxation effects play a major role, the interpretation of ligand K-edge XAS data in terms of electronic states (or multiplets) is more adequate. In these situations, it is necessary to compute the transitions to the different ligand-field and VBCI multiplets in the excited states that are electric-dipole allowed from the ground-state multiplet. For example, in the VBCI description of bonding discussed in the previous section, which is already set in terms of states (and not orbitals), the number of excited states ($\Psi_A$ and/or $\Psi_B$) is further expanded (e.g., $\Psi_A\{\Gamma_1, \Gamma_2\}$ and/or $\Psi_B\{\Gamma_1, \Gamma_2\}$) when ligand field (LF) effects are included (Figure 2.12).

The analysis of the Cl K-edge XAS data described in Chapter 6 of this thesis has been performed using the single-particle model. However, the potential of a multiplet-based methodology (Sections 4.3.2), implemented in a new Matlab-program (Section 6.1.4) to allow for differential orbital covalency determinations, is discussed and proposed for future efforts in ligand K-edge XAS spectroscopy (Chapter 7).

### 2.4.5. Ligand K-edge XAS in other elements

Cl K-edge XAS and S K-edge XAS are very well developed techniques that allow not only the evaluation of the energy splitting among the different low-lying empty
molecular orbitals, but also the covalency of M-Cl and M-S bonds. In the case of ligand K-edge XAS for other elements, the situation is different. Of particular interest, in the pursuit of a multi-edge study of ruthenium carbene-based catalysts, C K-edge XAS data have been successfully collected for most of the compounds listed in Chart 1.1. However, the determination of absolute covalencies for Ru-C bonds in this series is not possible at this point. Model complexes for which M-C covalencies are evaluated by other experimental techniques are necessary in order to calibrate the obtained results by XAS. Regardless of this inconvenience, the obtained spectra are still very useful for finding trends in the relative covalencies along the series of ruthenium catalysts considered here, as discussed in Chapter 6.

2.5. METAL L-EDGE X-RAY ABSORPTION SPECTROSCOPY

Metal L-edge XAS generally refers to an experimental XAS-based technique involving the L2 and L3 edges. The metal L1 edge, which results from the core 2s orbital in the metal to metal nd-based low-lying molecular orbitals, is electric dipole forbidden and hence is often neglected.

The L3 and L2 edges involve the transition from the 2p level to the metal nd-based low-lying molecular orbitals ($nd \leftarrow 2p$). This process is split into two transitions, due to a relatively large split-orbit coupling within the 2p shell upon the core-hole formation. The total intensity of the normalised pre-edge features reflects the total metal contribution in the low-lying empty molecular orbitals and it constitutes a secondary, independent probe (additional to metal K-edge XANES, Section 2.3) of the charge in the metal (135).

As opposed to ligand K-edge XAS spectroscopy, in metal L-edge XAS spectroscopy substantial changes occur during the formation of this core hole, so that electronic relaxation effects are far from being neglected. In addition to the strong 2p spin-orbit coupling, other important interactions to consider are the inter-electronic repulsion effects within the $nd$ valence shell and of the $nd$ shell with the core hole (in the case of the final state). Also, and although it is usually very small, the $nd$ spin-orbit coupling is often a relevant interaction to consider. More importantly, ligand field effects
and the possible interaction with other charge transfer configurations, which account for bonding interactions, are also considered.

The interpretation of metal L-edge XAS is often achieved by using a picture based on atomic multiplets (i.e., electronic states) rather than using a single-particle model, for which each observed peak in the pre-edge structure is interpreted as a transition to an empty molecular orbital (136). Unfortunately, based on the large number of interactions to consider, the analysis based on multiplets is very cumbersome.

Multiplet simulation programs are powerful tools that help in the interpretation and the extraction of information from Metal L-edge XAS data. The most commonly used in the field was written in FORTRAN 77 by Robert Cowan (137) and later updated by Theo Thole (138). Recent developments by Frank deGroot and Erik Wasinger (139) have allowed, to a certain extent, the estimation of what was termed differential orbital covalency, which consists of a projection method used to map out which multiplets originate from which orbital. The method employed is formally an approximation and is implemented within the Cowan programs as a very clever trick. As part of this thesis work, an ongoing project is the development of a new Matlab-based program that employs the VBCI + LF methodology implemented in Cowan, but with faster processing, user-friendly graphical user interfaces, and an improved model to assist in the extraction of differential orbital covalency (further details on this are given in Sections 4.3 and 6.1.4).

As an illustrative example, Figure 2.13 shows a simulated L\textsubscript{2,3}-edges XAS spectrum for a hypothetical, second-row transition-metal complex. The complex in this example has an octahedral symmetry and the ground-state configuration in the metal is Nd\textsuperscript{1} with the d-electron in a t\textsubscript{2g} orbital. Upon the generation of the multiplets in the final state (2p\textsuperscript{5}Nd\textsuperscript{2}), the major interaction, by far, is the spin-orbit coupling of the core hole in the 2p shell. Two families of multiplets, split by 3/2 ≤ 2p, are generated at this point: 2p\textsubscript{3/2}Nd\textsuperscript{2} and 2p\textsubscript{1/2}Nd\textsuperscript{2}. The interaction of the 2p core-hole multiplets with the Nd electrons is ignored. The coulombic interaction of the two electrons within the Nd shell (ee\textsubscript{Nd}) is introduced to give rise to the same set of \textsuperscript{2S+1}L multiplets in each of the branched 2p\textsubscript{j} states. The spin-orbit coupling of the electrons in the Nd shell is also
ignored and the octahedral ligand field (LF) is applied as a perturbation to the Nd atomic multiplets, $^{2S+1}L$ of each $2p_j$ branch. Under these considerations, the same set of LF multiplets emerge in each of these $2p_j$ branches, but with populations in the $2p_{3/2}$ set doubling those int the $2p_{1/2}$ set.

Under this formalism, the ground state in this example corresponds to $^2T_{2g}$. In the octahedral symmetry, the electric-dipole operator transforms as $T_{1g}$, and hence, the only electric-dipole allowed transitions are to multiplets with $T_{1g} \otimes T_{2g} = A_{1g} + E_g + T_{2g} + T_{1g}$ symmetry in the final state. Among these allowed transitions, the ones corresponding to LF multiplets (in the strong-field representation) with symmetry $^3T_{1g}(F)$, $^1T_{2g}(D)$, $^1E_g(D)$ and $^1A_{1g}(G)$ are projected to transitions to a $t_{2g}$ orbital, whereas the transitions to the LF multiplets with symmetry $^3T_{2g}$, $^3T_{1g}(P)$, $^1T_{1g}$, and $^1T_{2g}(G)$ correspond to transitions to an $e_g$ orbital. The allowed transitions to the $2p_{3/2}$- and $2p_{1/2}$-branched LF multiplets produce the $L_3$ and $L_2$ pre-edge bands in the final spectrum, respectively (Figure 2.13).

From the two interactions that were ignored in the example shown in Figure 2.13, at least the spin-orbit coupling of the Nd-shell, along with other ligand field symmetries need to be considered in the multiplet simulation of real compounds.

Moreover, other charge transfer configurations can be included in the simulation using a VBCI formalism to account for electronic relaxation effects and to additionally quantify for back-bonding (135), if present.

In particular, for the analysis of the Ru L$_{2,3}$ edges XAS data for the compounds listed in Chart 1.1, the implementation of a novel multiplet methodology based on a strong-field representation basis set is introduced using a sample data set for compound 4a, as an example (Section 6.1.4). However, since CoLoMoS (the Matlab-based program used) is under development, a complete analysis of the Ru L-edge in compounds 1-7 is an ongoing effort. At this point, a unique model that succesfully fits the overlapping Cl K- and the Ru L-edges simulataneously (see 3.6.6 and 6.1.2), is used to quantify chlorine charge donation to ruthenium in these compounds, and no further interpretation on the Ru L-edge features is given.
Figure 2.13 Multiplet simulation for the L₂,₃-edges XAS Spectrum of a hypothetical, second-row transition-metal complex with octahedral symmetry.

2.6. EXPERIMENTAL SET UP

The XAS data processed and analysed in this thesis work were collected over a period of five years at essentially four different beamlines of SSRL at Stanford
Table 2.2 lists the general settings used in these beamlines. Additional details on these settings are provided in subsequent sections.

### 2.6.1. Beamline 7-3 settings

Beamline 7-3 of SSRL is a hard X-ray beamline dedicated mostly to the EXAFS analysis of biological samples. Both solid and frozen solution samples can be investigated on this beamline. The Ru K-edge data for most compounds in Chart 1.1 was collected at beamline 7-3.

The source of beamline 7-3 is a 20-pole wiggler magnet and its monochromator consists of a Si(220) double crystal. An ionisation chamber (IC(\(I_0\)), Figure 2.14a) is used to detect the incident X-rays (\(I_0\)) just before they hit the sample. A second ionisation chamber is used to measure the transmitted light (\(I_1\)) after hitting the sample. Each of these ionisation chambers is filled with argon or nitrogen. Inside the chambers, these gases form ions as a result of the interaction with the incident light. These ions, along with the free electrons produced, generate a voltage measured by the electrodes inside the device.

The sample itself, at approximately a 45° angle in relation to the x-ray beam, is positioned inside a vacuum chamber that is cooled with an Oxford-Instruments CF1208 continuous-flow liquid helium cryostat below 20 Kelvin, to minimise the photoreduction of sensitive samples (Figure 2.14b). The emitted light is detected using an array of highly pure germanium (HPGe) crystals, which are kept under liquid nitrogen (140, 141). Every germanium crystal in this array constitutes a fluorescence detector channel on its own.

An additional ionisation chamber is used to measure the radiation (\(I_2\)) transmitted from a reference that is put after the second ionisation chamber measuring \(I_1\) (Figure 2.14a). This reference functions as an internal calibrant.
Figure 2.14 Experimental set up inside the hutch of beam line 7-3 of SSRL: (a) Front, (b) top and (b) side view.
Table 2.2  General settings for SSRL beamlines used to collect the data relevant to this thesis work.

<table>
<thead>
<tr>
<th>Beamline</th>
<th>7-3</th>
<th>6-2</th>
<th>4-3</th>
<th>10-1</th>
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<td>2360-2000</td>
<td>2400-14000</td>
<td>250-1200</td>
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<td>Ru K-edge</td>
<td>Cl K-, Ru L₂,₃- &amp; P K-edges</td>
<td>Cl K- &amp; Ru L₂,₃- edges</td>
<td>C K-edge</td>
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<td>~10⁻⁴</td>
<td>10⁻⁴</td>
<td>~2x10⁻⁴</td>
</tr>
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<td>Source</td>
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<td>56-pole, 0.9-Tesla Wiggler</td>
<td>20-pole, 2-Tesla Wiggler</td>
<td>30-pole, 1.45-Tesla Wiggler</td>
</tr>
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<td>Si(111) double crystal</td>
<td>Si(111) double crystal</td>
<td>6m SGM</td>
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<td>Incident radiation detector</td>
<td>Ionisation chamber</td>
<td>Ionisation chamber</td>
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<td>Fluorescence 13 or 30 element array HPGe</td>
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<td>Fluorescence Lytle ionisation chamber</td>
<td>CEM</td>
</tr>
</tbody>
</table>

2.6.2. Beamline 6-2 settings

Until a few months ago, beamline 6-2 was a soft X-ray beamline dedicated to performing experiments with emphasis on samples with biological importance. At the beginning of this year, however, the settings on this beamline have changed significantly to accommodate other experiments that were previously limited or non-existent on SSRL. Most of the XAS data on the Cl K-, and Ru L₂,₃-edges were collected in that beamline and only very recently the remaining data on these edges were collected at the brand new 4-3 beamline. The 4-3 beamline can be considered the "new 6-2 beamline," since their settings are practically the same. Therefore, only the details for beamline 6-2 will be given in this thesis.

The photon source for beamline 6-2 is a 56-pole wiggler magnet and a Si(111) double-crystal monochromator. For the collection of XAS data on solid samples, a set of two ionisation chambers was used to respectively measure the signals in I₁ (transmitted) and I₀ (incident) radiation in a similar way as in beamline 7-3 (Section 2.6.1). However instead of argon or N₂, helium gas was used in this case. Alternatively, a yield detection mode was also available with the use of a Lytle ionisation chamber detector operating with N₂ (140). This device measured the fluorescence (FF) coming
from the sample. The sample was held at approximately a 45° angle with respect to the incident beam under N\textsubscript{2} at room temperature inside a sample box. Separated only by an aluminum window, the Lytle FF detector is physically attached to the sample box (Figure 2.15). The incident X-ray beam not only interacts with the sample, but also with the N\textsubscript{2} present inside the sample box. Therefore, the role of the aluminum window is to filter the lines emitted by the N\textsubscript{2} upon relaxation. Hence, only the remaining lines coming from the sample are detected by this N\textsubscript{2} ionisation chamber detector. Contrary to beamline 7-3, in 6-2 (or 4-3) there was no active ionisation chamber detector for I\textsubscript{2} that in theory would result from the transmission from a second sample used as an internal calibrant. Under the range of operation of this beamline, the cross sections are higher than in a hard X-ray beamline like 7-3. Consequently, a considerable amount of radiation is not expected to be available for the reference. Instead, an external calibration procedure is performed by collecting a scan from a reliable calibrant material before and after the XAS data collection for the sample.

2.6.3. Beamline 10-1 settings

10-1 is a beamline dedicated to soft X-ray experiments. The operational range of energy for the X-rays used in this beamline is between 200-1200 eV. At these relatively low energies, the molecules in air (or even helium atoms) have a very large absorption cross section. Therefore, experiments in beamline 10-1 need to be performed in a chamber under ultra high vacuum (UHV) conditions (P <10\textsuperscript{-7} mmHg). As opposed to beamlines 6-2, 4-3 and 7-3, which handle harder X-rays, beamline 10-1 does not require the use of a hutch. This hutch protects the user from the exposure to X-rays, but since the X-rays in 10-1 propagate under vacuum, its use is unnecessary. Another important difference is that the settings are more flexible and, to a certain extent, more user-defined in this beamline. Depending on the kind of experiment to be performed, a number of different chambers are available for users. To collect the XAS data on the C K-edge, a small UHV chamber, built by Hodgson's group at SSRL, was used. The settings for 10-1 within this chamber are illustrated in Figure 2.16.
The source on this beamline is a 30-pole wiggler magnet and it uses a spherical grating monochromator (SGM) with 600 or 1,000 lines/mm. To measure the intensity of the incident beam ($I_0$), a gold-grid ring transversally positioned with respect to the incident X-rays is used. Additionally, and contrary to the settings on other beamlines
discussed here, no transmission mode detector is available due to technical difficulties regarding the sample preparation when using soft X-rays.

**Figure 2.16** Experimental set up inside the used UHV chamber at beamline 10-1 of SSRL: (a) Top and side views; (b) Components of the channeltron detector; (c) shower of electrons produced inside the channeltron from a single incident electron.

A thickness in the sample of 0.1 \( \mu \text{m} \) or less would be required to get a good transmission signal (105). Instead, a yield detection mode is pursued by the use of a channeltron or *channel electron multiplier* (CEM). A channeltron is a horn-shaped
device that amplifies the production of electrons. It is a dynode structure coated inside with an electron-emissive material. A difference of potential of about 2 kV is applied and a single electron hitting the conical entrance of the channeltron creates secondary electrons that eventually lead to the production of a shower of electrons, all collected by an anode at the other end of the device. The location of the device inside the chamber is at a 90° angle with respect to the incident beam (Figure 2.16b). The sample, whose position can be adjusted by rotating the sample holder, is positioned at a 45° angle with respect to the beam and the channeltron, so that the electrons produced due to the incidence of the X-rays can be detected and amplified. As in beamlines 6-2 and 4-3, the use of an internal calibrant is not possible and, again, XAS data is collected using an external calibrant.

2.6.4. Digitalisation of output signals

The output signal from any of the detectors considered in the previous sections is in the form of a current measured in amperes. Each of these signals is amplified and transduced as voltage pulses using a Keithley current amplifier device. The output of this device is further transduced by a hex scaler (or pulse counting device) that ultimately digitalises the signal in the form of frequency pulses.

2.7. DATA REDUCTION AND ANALYSIS

The data sets collected in the form of $I_1$ or FF are normalised with respect to the $I_0$ data automatically and directly at the workstations of any of the beamlines of SSRL. The resulting raw data set $I_1/I_0$ (or $FF/I_0$) is inspected at the time of its collection, to detect undesired scans due to a faulty setup, insufficient sample, or too much sample, leading to self-absorption or anisotropic effects (Section 2.7.5); to check for possible photoreduction processes in the sample (decomposition); and to determine if a good number of scans have been obtained to reduce the noise level by means of averaging the accumulated data scans. For the ruthenium carbene complexes considered for this thesis, two to four scans from each sample were collected.

To properly analyse the raw spectra, several processes need to be performed, typically in the following order: calibration and averaging, background subtraction,
normalisation and fitting. A brief description of each of these steps, as they are typically performed, is given in Sections 2.7.1-2.7.5. Additional details (some of them more particular) can also be found in the following chapters.

### 2.7.1. Calibration and averaging

By comparing the pre- and post-sample calibration scans, the calibration of sample scans is performed by a linear shift adjustment that is applied to all of the energy data points of a particular raw data scan. As stated before, the data collected in beam line 7-3 does not require a pre- or post-sample calibration scan since a calibration scan is taken at the same time as the sample is being swept. Furthermore, and prior to the calibration of a particular scan in that beamline, it is necessary to average the normalised data \((FF/I_0)\) that is collected from every germanium crystal in the detector array. For any other beam line, a single FF data set is obtained and this averaging step is unnecessary.

For the data obtained on the Cl K- and Ru L\(_{2,3}\)-edges (collected together), the calibrant used is the very well XAS-characterised Cs\(_2\)CuCl\(_4\). The peak maximum for the intense pre-edge feature for this compound (Figure 2.17) is at 2820.2 eV, and is used to perform the necessary energy adjustments. In the case of Ru K-edge XAS data, the reference used was ruthenium foil. The inflection point of the ionisation edge of the observed XAS for this material is assigned a value of 22117 eV (Figure 2.17) and used to adjust (if necessary) the energy scale of all the Ru K-edge XAS data scans. Finally, the C K-edge XAS data sets were proven to be the easiest to calibrate. The first minimum of a double well that is observed at 284 eV in the \(I_0\) data collected during any scan of any of the samples, is used (Figure 2.17). This double well is due to the absorption of multiple carbon-containing items in the chamber or in beamline 10-1 itself.

In a second data reduction step, the calibrated scans obtained for the same sample are simply averaged for the main purpose of reducing noise levels. The data obtained this way exhibit a background that is mainly imposed by the beamline settings and that is fitted and traditionally removed using the methodology discussed in the next section.
Figure 2.17 Reference used in the calibration of XAS data. (a) C K-edge, (b) Cl K-edge and (c) Ru K-edge. The dotted line denotes 1) the value of energy and 2) the specific spectral features that were used as reference in each case.
2.7.2. **Background removal and normalisation**

Bending magnets and insertion devices do not produce a homogenous radiation profile in the sense that not all wavelengths are produced with the same intensity. This implies a non-zero background in the $I_0$ signal that needs to be accounted for. Additionally, and as was described briefly in Section 2.2, an edge jump can correspond to essentially an accumulation of peak-like features that correspond to transitions to the different states in the continuum. During the fitting procedure, the edge jump is traditionally modeled using an arctangent (cumulative Lorentzian) or a cumulative pseudo-Voigt (Lorentzian + Gaussian) function profile (Section 2.7.4). This edge jump model is accurate if the collected energy range is small. However, the edge jump over an extended region of energy beyond the ionisation starts to decay slowly, having an additional influence over the background imposed by the incident beam. In other words, in the region near the edge, the background generally seems to change its steepness and sometimes even its shape.

Based on the previous discussion, in simple cases (i.e., in cases with a single edge), traditional approaches subtract two different backgrounds: typically, a linear, a smooth quadratic polynomial or a Gaussian background before the edge, and a quadratic-polynomial spline after it. The obtained spectra are normalised such that the post-edge plateau is set to an intensity of one. After the point of normalisation (without fitting), only a qualitative comparison with other spectra is possible. Additional fitting procedures, however, are necessary in order to deconvolute all of the features in the spectrum. In general, all these procedures are notoriously challenging and are not applied or performed uniformly in the field.

2.7.3. **Background models for multi-edge XAS analysis**

Background subtraction in metal L-edge XAS is particularly challenging. The two closely related edges ($L_3$ and $L_2$) usually influence significantly the change in the background more than once. Again, there is not a consensus on how this background should be removed from the data in order to have less influence in the other, more meaningful, spectral features. A recurrent practice is to subtract the background in the region prior to the first edge and subsequently the one after the first and before the
second edge. In this approach, a second-order polynomial spline is used to fit the region after the second edge and a point is used in this region to undergo the normalisation procedure.

Figure 2.18 Effect on the steepness of the quasi-linear regions ($m_j$) upon subtracting a single linear background ($f_1$) to a multi-edge XAS data set.

In the analysis of the Cl K- and Ru L$_{2,3}$-edges of ruthenium-based carbene catalysts (Chapter 6), we have encountered important obstacles. One of them is the clear and very distinct influence that each edge has on the background. Figure 2.18 illustrates the effect of subtracting, for example, a single linear polynomial function to a Cl K- and Ru L$_{2,3}$-edges XAS spectrum corresponding to the first-generation Grubbs catalyst (1a, Chart 1.1). The resulting data set hardly posses flat plateaus in the third and second quasi-linear regions of the spectrum ($m_2 \neq 0$ & $m_3 \neq 0$). From these results, it was clear that a robust method was necessary to effectively background-subtract well-established and tested models to these and other similar data.

In 2006, a methodology to normalise multi-edge spectra was reported (1). The methodology included the use of a background in a functional form given by Equation

\[ f_1 \]

\[ Data \]

\[ Data - f_1 \]

\[ m_1 \rightarrow 0 \]

\[ m_2 \neq 0 \]

\[ m_3 \neq 0 \]

\[ \text{Energy} \]

\[ \text{Intensity} \]
2.6. Every term of the summation in this expression contains a parent function (with corresponding corrected Y intercepts) that is multiplied by a factor coefficient. This factor coefficient is a weighting functional dependent on the energy position.

**Equation 2.6**  The handle-like background model.

\[
f_{hlb} = \sum_{j=1}^{n} f_j \cdot a_j = \frac{\sum_{j=1}^{n} f_j \cdot \frac{1}{|X-V_j|}}{\sum_{j=1}^{n} \frac{1}{|X-V_j|}}\]

Where,

- \(f_{hlb}\) = Handle-like background model function
- \(f_j\) = Y-Intercept-corrected Parent function for the \(j\)-th quasi-linear region
- \(a_j\) = Factor coefficient for the \(j\)-th quasi-linear region
- \(V_j\) = Pivot energy parameter in the \(j\)-th quasi-linear region
- \(X\) = Energy "vector" in original data set

Figure 2.19 shows the relationship between parent functions \((f_n)\) and Y-intercept-corrected parent functions \((f'_n)\) for the \(n\)-th region in a double-edge XAS spectrum with three quasi-linear regions. The corresponding corrections for the Y-intercept, \(C_n\), are calculated using Equation 2.7. Since the change in the background is partially due to the edge jump, the values of energy at which the correction coefficients \((C_n)\) are evaluated are ideally chosen to be the inflection point of the edges \((I_j)\).

Pivot parameters in this model \((V_j)\) modulate the transition from the parent function of one region to another; they are not known \textit{a priori}, and therefore are set as the solution parameters of a solver optimisation in Microsoft Excel®. Within this optimisation, the pivot parameters \((V_j)\) are adjusted so that the sum of absolute values of the slopes \((m_j)\) that fit the quasi-linear regions in the background-subtracted data set (Equation 2.8), gets minimised (Figure 2.20). Due to the resemblance of the model function described here to the operation of a "handle," it has been termed in a recent publication as the "handle-like" background model (141).
The handle-like background was developed originally to fulfil the traditional agenda of background subtraction prior to normalisation and fitting. Therefore, the values on the inflection point for the edges (used to correct the Y-intercept) as described above are not known \textit{a priori}. Consequently, when using the handle-like model exclusively for background subtraction, a good approximation is the use of the inflection points reported in the literature for the natural form of the transition metal (or group of elements) responsible for the multiple-edge XAS spectra studied.

A more recently developed background model \textit{(141)} is more suitable for fitting procedures (and was originally developed as such). This model, termed recently as the "switch-like" model, significantly reduces the number of parameters and provides a more physically meaningful background by linking some of its parameters to those in an edge jump.
Equation 2.7  Adjustment for the Y intercept in the \( n \)-th quasi-linear region function \( f_n \).

\[
C_n(I_j) \equiv b'_n(I_j) - b_n = \begin{cases} 
0, & n=1 \\
\sum_{i=2}^{n} f_{i-1}(I_j) - f_i(I_j), & n \geq 2
\end{cases}
\]

Where,

\( C_n \) = Y intercept adjustment for the \( n \)-th quasi-linear region

\( b'_n \) = Corrected Y intercept for the function in the \( n \)-th quasi-linear region

\( b_n \) = Y intercept for the function in the \( n \)-th quasi-linear region

\( f_i \) = Parent function in the \( i \)-th quasi-linear region

\( I_j \) = inflection point in the \( j \)-th edge

Equation 2.8  Linear least-squares fitting of linear model functions to the quasi-linear regions of the backgroud subtracted data set. The minimisation of \( G \) by the adjustment of the pivot parameters, is subjected to the additional condition that the sum of the absolute values of the slopes, \( m_j \), has to be minimised itself (Figure 2.20).

\[
G = \sum_{j=1}^{n} \sum_{i=\alpha_j}^{\beta_j} \{(Y(i) - f_{hlb}(i)) - (m_j X(i) + b_j)\}^2
\]

Where,

\( G \) = sum of squared errors between the subtracted data and linear model functions evaluated on the quasi-linear regions from \( j=1 \) to \( n \)

\( \alpha_j, \beta_j \) = quasi-linear region data delimiters

\( X \) = Energy "vector" in original data set

\( Y \) = Intensity "vector" in original data set

\( f_{hlb} \) = handle-like background function

\( m_j, b_j \) = slope and Y intercept of linear model function in the \( j \)-th region
Figure 2.20 Subtraction of the handle-like model ($f_{hlt}$) to a multiple-edge XAS data set.

The functional form of this new model is given by Equation 2.9. As in the case of the handle-like model, each term in this summation is constituted by the parent function corresponding to a particular quasi-linear region (with adjusted Y intercept) and by a factor, which in this case is a set of two unit step functions that act as switches. The first unit step function switches "on" the parent function above a given value of energy ($I_{1,i}$) whereas the second one switches "off" the same function above a second, higher value of energy, $I_{2,i}$.
Equation 2.9  The switch-like background model.

\[ f_{slb} = \sum_{i=1}^{n} f_i \cdot a_i = \sum_{i=1}^{n} f_i \cdot u(X - I_{1,i}) \cdot u(I_{2,i} - X) \]

Where,

- \( f_{slb} \) = Switch-like background model function
- \( f_i \) = Y-Intercept-corrected parent function for the i-th quasi-linear region
- \( a_i \) = Factor coefficient for the i-th quasi-linear region
- \( u(x - c) \) = Heaviside unit step function
  \[ u(x - c) = \begin{cases} 
    0, & x < c \\
    1, & x > c \\
    u_0, & x = c
  \end{cases} \]

- \( I_{1,i}, I_{2,i} \) = Switch delimiters for the i-th quasi-linear region function, \( f_i \)
  with \( I_{2,i} = I_{1,i+1} \)

- \( X \) = Energy ”vector” in original data set

To provide a smoother change between background functions, the formal definition of the unit step function is not used, but instead a variation to the Fermi-Dirac-Boltzmann distribution function as a close approximation (Equation 2.10). This approximation makes use of an additional width parameter (\( w \)) that ultimately provides the ”rate” at which the parent functions change. Figure 2.21 illustrates the relationship between \( w \) and \( \gamma \), defined here as the half-width at half the maximum (hwhm).

As stated in the previous section, the change in the background steepness and shape on raw XAS spectra is somewhat associated with effects due to the ionisation edge. Consequently, when building a background model, parameters \( I_{1,i} \) and/or \( I_{2,i} \) can be linked to the inflection point of specific edge jump functions (see additional details in Section 3.4.1). Moreover, the width of the edge jump, which is usually expressed in terms of \( \gamma \) (hwhm), can also be linked to the same parameter \( \gamma \) in the switch-like background. This is represented graphically in the example illustrated in Figure 2.22.
Equation 2.10  Approximation to the unit step function using the Fermi-Dirac-Boltzmann distribution profile using either an additional generic width ($w$) parameter or the half width at half the maximum ($\gamma$).

$$u(x - c) \approx \frac{1}{1 + e^{\frac{c-x}{w}}} = \frac{1}{1 + e^{\frac{(\ln 3)(c-x)}{\gamma}}}$$

Where,

$$u(x - c) = \text{Unit step function}$$

$$w = \text{Width}$$

$$\gamma = \text{Half width at half the maximum (hwhm)}$$

Figure 2.21  Relationship between the generic width parameter ($w$) and $\gamma$ (hwhm) in the approximation to the unit step function, using the Fermi-Dirac-Boltzmann profile.

\[
\frac{1}{1 + e^{\frac{I-x}{w}}} = \begin{cases} 
\frac{1}{4}, & I - x = \gamma \Rightarrow e^{\gamma/w} = 3 \\
\frac{3}{4}, & I - x = -\gamma \Rightarrow e^{-\gamma/w} = \frac{1}{3} 
\end{cases}
\]

$$w = \frac{\gamma}{\ln 3}$$
Figure 2.22 Linkage of parameters in the switch-like background ($f_{\text{slb}}$) to related parameters in an edge jump function ($f_e$).

Note how only one switch is necessary per parent function when dealing with single-edge XAS data (the same is true for the "extreme" parent functions in a multi-edge situation). This is because the corresponding values of $I_{1,1}$ and $I_{2,2}$ in the "missing" switch functions are set to $-\infty$ and $+\infty$ respectively. The values of $I_{2,1}$ and $I_{1,2}$, on the other hand, are set as the inflection point ($I$) of the edge jump.

As demonstrated graphically in Figure 2.22, the switch-like background model can be used not only in multiple-edge cases, but also in simpler cases that only involve a single-edge. Its implementation within a fitting routine is discussed in the next chapter.
2.7.4. Conventional fitting procedures

A final step in the analysis of XAS data is the fitting procedure. It involves the fitting of a theoretical physically meaningful model to the data. Each individual feature in the normalised spectrum is modeled using a particular function. The energy position of each of these features is approximately determined by the second derivative of the data. The second derivative also provides the number of features, and hence the number of model functions to use to fit the data.

The Dirac delta function in Equation 2.2 produces an infinitely-thin spike of infinite intensity at resonance conditions. This represents the interaction of matter with a periodic potential for which the excited state has an infinite lifetime (142). However, the uncertainty principle itself imposes a finite natural lifetime (137). Therefore, under quantum mechanical considerations, the transition probability can be reformulated (105, 143, 144) as the intensity distribution function (with finite height and width) given by Equation 2.11.

Equation 2.11 Normalised Lorentzian distribution function.

\[
L = \frac{1}{\pi} \times \frac{\gamma}{(E' - E - h\nu)^2 + \gamma^2}
\]

Where,

- \(L = \text{Lorentzian distribution function}\)
- \(E' = \text{Excited state energy}\)
- \(E = \text{Ground state energy}\)
- \(h\nu = \text{Incident radiation energy}\)
- \(\gamma = \text{half width at half maximum}\)

In this expression, known as the Lorentzian distribution function, \(\gamma\) (hwhm) accounts for the natural broadening of the transition with a given finite lifetime. This natural broadening can be further enhanced by the fact that absorbing atoms are not
isolated, but instead coupled together by the radiation field, providing additional pathways for relaxation and hence further reduction of lifetimes.

In addition to natural broadening, transition lines are subject to other sources of broadening effects (including the instrumentation), some of which cause the intensity of such lines to distribute as in a Gaussian distribution (Equation 2.12).

**Equation 2.12**  Normalised Gaussian distribution function.

\[
G = \sqrt{\frac{\ln 2}{\gamma^2 \pi}} e^{-\frac{(\ln 2)(E' - E - h\nu)^2}{\gamma^2}}
\]

Where,

- \( G \) = Gaussian distribution function
- \( E' \) = Excited state energy
- \( E \) = Ground state energy
- \( h\nu \) = Incident radiation energy
- \( \gamma \) = half width at half maximum

Both of these profile line shapes (Lorentzian and Gaussian) are present in a real spectrum, as the convolution of the two distribution functions. The intensity distribution given by the obtained profile is called a Voigt distribution function. A variation of this function is the so-called pseudo-Voigt profile for which a simple weighted sum of Gaussian and Lorentzian distribution functions is used (Equation 2.13). The weighting coefficient, \( c_g \), helps to modulate the shape from a 100% Gaussian (\( c_g = 1 \)) to a 100% Lorentzian (\( c_g = 0 \)) shape.

The use of Lorentzian, Gaussian, Voigt or pseudo-Voigt profiles is very common in spectroscopy to model the line shapes of transitions within a peak fitting routine. A similar approach is used to model edges. However, an ionisation edge involves a continuous number of transitions and therefore, to model an edge jump, instead of using a single transition line shape model, a cumulative version of these distribution functions is used (Figure 2.23).
**Equation 2.13**  Weighted pseudo-Voigt distribution function.

\[ V_P = (1 - c_g)L + c_gG \]

*Where,*

\[ V_P = \text{Pseudo-Voigt distribution function} \]
\[ L = \text{Lorentzian distribution function} \]
\[ G = \text{Gaussian distribution function} \]
\[ c_g = \text{Gaussian weighting coefficient} \]

**Figure 2.23** Cumulative distribution functions and their profiles: (a) Cumulative Lorentzian (\( C_L \)); (b) Cumulative Gaussian (\( C_G \)); and (c) Cumulative pseudo-Voigt (\( C_{VP} \)) with weighting Gaussian coefficient, \( c_g = 0.5 \).

\[ C_L = \int_{-\infty}^{\hbar \nu} L \, dE_{\hbar \nu} = \frac{1}{2} \arctan \left( \frac{I - \hbar \nu}{\gamma} \right) + \frac{1}{\pi} \]

\[ C_G = \int_{-\infty}^{\hbar \nu} G \, dE_{\hbar \nu} = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{I - \hbar \nu}{\gamma / \ln 2} \right) \right] \]

\[ C_{VP} = (1 - c_g)C_L + c_gC_G \]

In typical fitting procedures for XAS data, the post-background-subtracted and normalised data are used. The smallest possible number of model functions for peaks and edges is considered to create an *evaluation function*. The intensities, widths, shapes and energy positions included in the evaluation functions are set as floating parameters that are optimised with respect to the XAS data using a non-linear least-squares optimisation approach. PeakFit® and EDG_Fit are two common software...
packages used by the XAS community to accomplish this task. But regardless of the software used, non-linear least-squares procedures with even a few parameters do not have a unique solution. The general approach, then, is to generate a handful of independent good fits and to report the results for the fitted parameters based on the average of this set of fits, and the error on them based on the corresponding standard deviation. There is, however, a large bias element involved while generating this set of mutually independent fits.

In the next chapter, a recently developed methodology is discussed along with its implementation in a new Matlab-based software package in order to reduce the bias associated with the generation of this family of independent fits. A fundamental part of this methodology is the inclusion of the switch-like background, along with an internal normalisation of the peak features, as part of the fitting model. This helps to reduce the propagation of errors and uncertainties that emerge by the performance of a successive number of steps in the original data.

2.7.5. Anisotropic and self-absorption effects in XAS and their implications on fitting procedures

The quantity of sample used, as well as the incidence angle of the X-rays, can both have an important impact on the obtained XAS data. Self-absorption is one of the important effects. Particularly, in cases in which a fluorescence detector is used, self-absorption can alter the shapes and widths of transition lines. When more than enough sample is employed, the light emitted by one atom may be reabsorbed by another atom, which may lead to a different decay pattern, perhaps through a lower level or collisional de-excitation, reducing in this way the overall intensity of fluorescence observed (137). Consequently, the transition line appears to be broader because of the flattening of the top of a peak, due to a larger effect towards the centre of the line.

Other problems can be observed in beamlines that employ channeltrons (such as in beamline 10-1). When more than enough sample is located at a particular spot in the sample, "charging" or saturation effects may occur due to the excess of charge that may build up in the sample due to a non-effective contact to the conductor or semiconductor material to which it has been stuck during the sample preparation.
Whenever this or any self-absorption problem has been encountered in a particular XAS data set, such data has not been considered for further analysis.

Another common problem, probably more difficult to control in some cases, is the observed direction dependence of spectral features due to the amount of sample. In situations in which a single edge is present, this is usually less of a problem since the pre-edge intensities compared to their corresponding edges remain more or less constant in sample-to-sample runs. However, in situations in which a double edge is present (e.g., Cl K- and Ru L_{2,3}-edges XAS), different runs on different samples alter the relative intensities of the different edges involved. In these cases, the incident X-rays are able to differentiate between the distinct angular momentum and atomic positions in the sample. In such cases, virtually every scanned sample exhibits even a slightly different fit (although, still substantially different when compared to fit-to-fit errors). To account for this effect, an average over several scans is reported when present, and only very obvious outliers are discarded and not included in the final analysis.

2.7.6. **Radiation damage**

Especially at lower energies and due to higher cross sections, the samples studied are in general prone to radiation damage, which in certain cases may be severe. A relatively easy and effective way to detect such effects consists in the collection of multiple quick scans of the same sample. When radiation damage is present, different features in the spectra should be changing in relative intensity over time.

Fortunately, with the exception of compounds 3a and 3b, which exhibit decomposition only in the Cl K-edge region, no other compounds at any other region were prone to radiation damage.
CHAPTER 3: BLUEPRINT XAS

Blueprint XAS is a Matlab-based program developed to fit and analyse XAS data, most specifically in the near-edge region of the spectrum. The program is based on a recently developed methodology that introduces the switch-like background function (Equation 2.9) into a holistic fit model that is capable of generating any number of independent fits. Importantly, and even though the program and methodology are tailored to XAS users, it can be used to solve any fit-related problems in any research field.

3.1. MOTIVATION

As discussed earlier, among the ligand K-edge XAS techniques, Cl K-edge XAS is probably the most developed and robust technique that, in principle, should be relatively straightforward to analyse. However, a major obstacle that delayed the research on the Grubbs catalysts for several years was the overlapping Cl K- and the Ru L_{2,3}-edges. This particular problem extends elsewhere, from recently investigated compounds with anti-cancer activity (145) to other ruthenium and chlorine containing compounds. This is a problem without a simple solution. A proper and thorough analysis requires that the region after an edge jump be relatively clean (other than the EXAFS structure), so that it can be properly normalised. This step is crucial to determine covalency and to compare results among different compounds. An additional problem was the challenging background, as discussed previously (Section 2.7.3).

In early attempts to analyse some preliminary Cl K- and Ru L_{2,3}-edges XAS data, the handle-like background was proven to be a very useful model to undergo the background-subtraction procedure. Furthermore, under the assumption that the ratio between the intensity of the two Ru (L_2 and L_3) edges was a constant from compound to compound, the corresponding value obtained from the spectrum of compound 8 was used to normalise the XAS data for the rest of the compounds. However, the spectra collected at different times from different samples on the same compound showed that, even though the shape of spectral features was identical, the Ru L_{2,3} branching ratio
was not a constant. This situation left the overlapping problem unresolved until very recently (see further details on Chapter 6). Importantly, it was also crystal clear at that point that fitting, normalisation and background subtraction, even in the simplest cases, are procedures prone to bias. Particularly in the case of fitting, it is easy to see that more than one physically plausible fit is possible. But, how many of these fits are required to statistically represent the solution to a particular fitting problem? And how can we be sure that all of the solution space has been covered by the number of fits created, being aware that bias plays a major role in choosing starting points prior to every fit?

Blueprint XAS was programmed using several ideas that evolved from all these questions and pitfalls in the data-processing procedures over a period of two years. The underlying goal was to improve the processes involved in the analysis of XAS by reducing user bias as well as the propagation of errors involved by the sequential execution of these processes.

Blueprint XAS relies heavily on optimisation and statistics algorithms implemented within Matlab. Programming in Matlab is relatively easy compared with using other traditional languages, such as C/C++ or Fortran. It requires less programming experience due to its high-level programming language, which allows the user to work with built-in functions in a user-friendly, object-oriented programming environment. Hence, most of the time invested in the development of Blueprint XAS was devoted to writing the code and actually developing the methodology detailed in the next sections, rather than the exhaustive task of learning a low-level programming language.

### 3.2. UNDERLYING METHODOLOGY ENCODED IN BLUEPRINT XAS

As in any other traditional approach, in an initial setting-up step, the user must define an *evaluation function*, which is the physical model used to fit a particular data set. An initial guess on each of the parameters of this evaluation function also helps the user define upper and lower limits.

As opposed to traditional methods, in order to minimise the propagation of errors associated with a pre-fitting background removal, the background is included as part of
the evaluation function (in addition to functions modeling peaks and edges). The switch-like background model, whose parameters can be linked to parameters in one or several edges, is most suitable to this approach.

In addition to the inclusion of the background to the fitting model, two main characteristics are unique to this methodology:

1) A large, user-defined number of fits are generated.

2) The starting points that lead to these fits are not user-defined, but instead selected from a Monte-Carlo based search procedure. This procedure involves an array of 1,000 randomly generated parameter combinations spanned through the entire solution space, which is delimited by the upper and lower bounds in every parameter. The sum of squared errors (SSE) (Equation 3.4, Section 3.3.2) is calculated for each of these combinations and the one with the smallest SSE value is selected as the starting point. This start point is then passed as part of the input to a non-linear least-squares (NLLS) curve-fitting procedure (Section 3.3.1) from which a fit is computed. Importantly, a new array of 1,000 parameter combinations is generated prior to the selection of the start point used for the computation of the next fit (see Figure 3.1).

In principle, this methodology is intended to reduce user bias towards certain values in the fitting parameters. Therefore, the upper and lower limits selected for every parameter need to be as distant, one to the other, as is physically possible to ensure that the whole relevant solution space of the fitting problem has been explored.

Another important goal of this methodology is the estimation of errors. In Blueprint XAS, the array of resulting fits, as well as the corresponding array of start points that lead to each fit, are saved to the output for further analysis. Included in the output is a set of goodness-of-fit parameters for each fit (Section 3.3.2).

The computed confidence intervals for every parameter in each fit are also included in this output. These confidence intervals, in principle, represent an estimation of the error associated with the computation of each fit. However, if a large number of fits is generated, the error associated with the fitting procedure is better represented by
the standard deviation of the coefficients in the whole population of fits. (The error associated with each fit is systematically removed upon the creation of a large family of them, as implied by Equation 3.10).

**Figure 3.1** Computer algorithm for Blueprint XAS.

![Flowchart](image)

Figure 3.2 illustrates, with the use of a simple example, the methodology described above. The example consists of the fitting of a data set using a linear evaluation function with parameters \( m \) (Slope) and \( b \) (Y Intercept). The upper and lower bounds for \( m \) are set as \( 1 \times 10^{-2} \) and \( 1 \times 10^{-3} \), respectively. The corresponding limits for \( b \) are set as -25 and -5. Since the example is simple enough, a surface can be created using a *discrete*, but large number of combinations of \( m \) and \( b \). The z-component of each point in the obtained mesh grid is defined as the corresponding \(-\log(\text{SSE})\) value and estimated upon the comparison of the evaluation function with the data using the corresponding values of \( m \) and \( b \) at each point of the mesh. The solution to this particular problem sits on the maximum of the surface in Figure 3.2a. From this, it is also evident that there is a strong anti-correlation relationship between parameters \( m \) and \( b \), as indicated by the belt of "peaks" at high values on \(-\log(\text{SSE})\).
Figure 3.2 Fitting of a straight line (with added random noise) using the methodology described in the text. (a) Solution via the evaluation of the fitting model using a discrete number of values of \( m \) and \( b \). (b) Selection of the start point (black triangle) (out of a 1000 randomly generated points; grey dots) used in the computation of the first fit. (c) Selected start points used in the computation of 100 fits (black-hollow triangles) and the final fit in all cases (grey circle).

In a regular XAS fit problem, the creation of an equivalent surface in order to find the solution (or solutions) is prohibitive (even in the simplest cases). Instead, Figure 3.2b and Figure 3.2c illustrate the application of the methodology described above to the linear function of this example. The surface of Figure 3.2a (seen from the top and
projected into the xy plane) is embedded as reference. A total of 100 fits are computed. The 1,000 random combinations of values of \( m \) and \( b \) for one of the fits (grey dots in Figure 3.2b) clearly span the whole solution space. From these combinations, that with the lowest SSE (or highest \(-\log(\text{SSE})\)) is selected as the start point (represented by the black solid triangle) in the computation of that particular fit. In Figure 3.2c, the selected start points for each of the computed fits are represented as black-hollow triangles. The fact that nearly all of these starting points lie on the anti-correlation belt region (with most of them near the solution) reflects the effectiveness of the Monte-Carlo based method in selecting reasonable start points - and confirms that the evaluation function is well behaved. Due to the simplicity of this example, the solutions of the 100 fits are practically identical and are represented by the dark-grey solid circle in Figure 3.2c. Additional demonstrative XAS examples are further discussed in Section 3.6.

### 3.3. CURVE FITTING AND MATLAB BUILT-IN FUNCTIONS

Blueprint XAS makes use of specific Matlab built-in functions to undergo the curve fitting procedures. Following is a brief description of these functions.

1) Function "fittype". It generates an object with a full description of the evaluation function and its parameters.

2) Function "fitoptions". It generates a structure containing all of the details on the parameters required to compute the fit. Several fit-option parameters are contained in this structure and passed on to Matlab through Blueprint XAS:

"Algorithm" corresponds to the NLLS curve fitting method to be used (see Section 3.3.1 for details).

"Exclude" is a vector of logicals of the same size as the data. Regions of the spectrum that are excluded for the fit are assigned values of one (or "true") in the corresponding matrix elements of the exclusion vector.

"DiffMinChange" and "DiffMaxChange" correspond respectively to the minimum and maximum change in the finite differences gradient.

"Lower" and "Upper" are vectors containing the lower and upper bounds for every parameter in the evaluation model. The "StartPoint" vector, which is another field of the
“fitoptions” structure, contains an initial guess but is only accessible through Blueprint XAS if the type of job is chosen to be "manual". Otherwise, internally, after the Monte-Carlo search subroutine selects the best start point out of a thousand, this vector is passed on to the “fitoptions” structure prior to the computation of every fit.

"MaxFunEvals", the maximum number of function evaluations, corresponds to one of the criteria used by Matlab to exit the fitting algorithm. Another criteria used is "MaxIter", the number of maximum iterations allowed inside the fitting algorithm. Additionally, termination tolerance parameters in the evaluation function (TolFun) and in the coefficients (TolX) are used as the criteria for convergence by Matlab.

"Robust" allows the use of a weighting factor for each data point as a way to systematically reduce the influence of possible outliers in the fitting procedure.

"Weights" is a vector with values between 0 and 1 that explicitly allows the user to deliberately impose a different weighting influence to the fitting procedure in different regions of the data.

3) Function "fit". It uses the "fittype" object as well as the "fitoptions" structure to fit the model to the data. The output of this function includes a "cfit" object from which the fitted parameters, their corresponding confidence intervals (at the level specified), and the evaluation function at the given data points are retrieved. Additionally, the goodness-of-fit parameters along with the residuals are also obtained and passed on to Blueprint XAS in the output.

To generate each fit presented in this thesis, the ‘fitoptions’ listed on Table 3.1 were used, unless indicated otherwise.

**Table 3.1** Default ‘fitoptions’ parameters used for the fitting of all the data analysed in this thesis.

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
<th>Parameter Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algorithm</td>
<td>Trust-Region</td>
<td>Robust</td>
<td>On</td>
</tr>
<tr>
<td>DiffMinChange</td>
<td>$10^{-8}$</td>
<td>DiffMaxChange</td>
<td>0.1</td>
</tr>
<tr>
<td>MaxIter</td>
<td>25,000</td>
<td>MaxFunEvals</td>
<td>75,000</td>
</tr>
<tr>
<td>TolFun</td>
<td>$10^{-6}$</td>
<td>TolX</td>
<td>$10^{-6}$</td>
</tr>
</tbody>
</table>
3.3.1. Non-linear least-squares curve fitting in Matlab

Linear least-squares optimisation methods are based on the minimisation of the sum of squared differences \( g \) between response data points \( (y_i) \) and the corresponding values in the evaluation function \( (f_i) \), with respect to the coefficient parameters \( (c_i) \), as described by Equation 3.1. A system of simultaneous linear equations, with a unique solution for every parameter \( c_i \), emerges if the evaluation function \( f \) is as simple as a polynomial or a power-based function. However, the situation is much more complex for any other evaluation function, such as the one required to solve a fitting problem in XAS. In such cases, non-linear least squares (NLLS) methods are required.

Three different NLLS algorithms are available in Matlab and are all accessible through Blueprint XAS: 1) trust-region, 2) Levenberg-Marquardt and 3) Gauss-Newton. According to the on-line documentation of Matlab, however, the Gauss-Newton algorithm should be only used for educational purposes. Hence, only the first two are recommended to solve actual fitting problems.

Both algorithms, the trust-region and the Levenberg-Marquardt, are Newton-step based methods for which a quadratic approximation to the objective function \( F \) is used (Equation 3.2). This approximation is accomplished by using a Taylor expansion around the current point, \( C_K \).
**Equation 3.1**  
Linear least-squares optimisation.

$$g = \sum d_i^2 = \sum (f_i(c_1, c_2, ..., c_j) - y_i)^2$$

**With,**

$$\frac{\partial g}{\partial c_1} = 0, \quad \frac{\partial g}{\partial c_2} = 0, ..., \quad \frac{\partial g}{\partial c_j} = 0$$

**Where,**

- $g =$ *sum of squared differences*
- $d_i =$ *difference between $y_i$ and $f_i$*
- $y_i =$ *response i-th data point*
- $f_i =$ *Evaluation function at the i-th data point*
- $c_1, c_2, ..., c_j =$ *Coefficient parameters in evaluation function, $f$*

At a given point of the optimisation for which the Hessian matrix $(H_K)$ is negative definite ($\delta TH\delta < 0$), the value of the parameter $\lambda$ is large enough to make $H'_K$ positive definite (a requirement to solve Equation 3.2). This makes the Newton step ($\delta$) size significantly smaller and with the direction of that of a "steepest descent" method, for which the direction of $\delta$ is the opposite to that of the gradient ($\delta=-\nabla F$). In the Levenberg-Marquardt algorithms, these measures make the optimisation process significantly slower, if stuck in a region with a negative-definite Hessian matrix.

On the other hand, the trust-region methods represent an evolution of the Levenberg-Marquart algorithms. In this case, the Newton step relies on the optimisation of the quadratic function $(Q)$ within a region of centre $C_K$ and radius $\Delta_K$, inside which the approximation of $Q$ to $F$ is valid. The algorithm proceeds with the additional restriction that the norm of $\delta \leq \Delta_K$. In case of a successful iteration, the trust-region expands its radius $\Delta_K$ for the subsequent steps of the optimisation; otherwise it gets contracted.

Moreover, in points at which the Hessian is negative definite, the norm of the Newton step size in trust-region methods becomes equal to the size of the trust radius ($||\delta|| = \Delta_K$), as a quick attempt to move to other more interesting regions.
Equation 3.2  Quadratic approximation to the objective function ($F$) in Newton-step based optimisation algorithms.

$$F(C_k + \delta, x) \approx Q(\delta, x) = F(C_k, x) + (\nabla_k F)^T \delta + \frac{1}{2} \delta^T H'_k \delta$$

Where,

$$F = \text{Objective function to optimise}$$

$$Q = \text{Quadratic approximation to the objective function}$$

$$C_k = \text{Vector of coefficient parameters at optimisation point } k$$

$$(\nabla_k F)^T = \text{Transpose of gradient of } F, \text{ computed at point } k$$

$$H'_k = \text{Approximation to the Hessian matrix of } F, \text{ evaluated at point } k$$

$$= H_k + \lambda I$$

$$H_k = \text{Hessian matrix of } F, \text{ evaluated at point } k$$

$$I = \text{Identity matrix}$$

$$\lambda = \text{Shift parameter}$$

$$\delta = \text{Newton step size}$$

$$= C_k - C_{k-1}$$

$$= -(H'_k)^{-1}\nabla_k F = -(H_k + \lambda I)^{-1}\nabla_k F, \quad (\nabla Q = 0)$$

$$(||\delta|| \leq \Delta_k, \text{ (in the Trust-region algorithm)})$$

$$\Delta_k = \text{Trust radius}$$

These considerations make the trust-region algorithms more robust for optimisations in general. However, in the context of curve fitting, the difference between the two is practically unnoticeable: the Hessian matrix is always positive definite due to the fact that the objective function $F$ is equal to the sum of squared differences, just as function $g$ in Equation 3.1.
Equation 3.3  Constrained evaluation function for Levenberg-Marquardt and Gauss-Newton algorithms, as implemented in Blueprint XAS.

\[ f'(c_1, c_2, ..., c_j) = f(c_1, c_2, ..., c_j) \times \prod_{i=1}^{m} u(c_i - L_i) \cdot u(U_i - c_i) \]

Where,

\[ f = \text{Evaluation function} \]
\[ f' = \text{Constrained evaluation function} \]
\[ c_1, c_2, ..., c_j = \text{Coefficient parameters in evaluation function, } f \]
\[ L_i = \text{Lower-limit bound for the } i\text{-th constrained coefficient parameter } c_i \]
\[ U_i = \text{Upper-limit bound for the } i\text{-th constrained coefficient parameter } c_i \]
\[ m = \text{total number of coefficient parameters constrained in } f \]

Nevertheless, there is an important difference between these two algorithms, as implemented in Matlab. Only the trust-region algorithm supports bound limits for the parameters in the evaluation function. In Blueprint XAS, however, the constrained optimisation using bound limits is possible using the Levenberg-Marquardt or the Gauss-Newton algorithms. To do this, Blueprint XAS multiplies the entire evaluation function \(f\) by a set of two Heaviside’s unit step functions \(u\), Equation 2.9) for each parameter that the user decides to constraint (Equation 3.3). Under these circumstances, the constrained parameters cannot lie outside certain range imposed by the given bounds, or else the whole function collapses.

3.3.2. Statistical criteria for curve fitting

In the context of least-squares methods, a fit is subject to the assumption that the deviations are randomly distributed around the evaluation function. In Blueprint XAS, the structure of the residuals is graphically displayed at all times. This in itself represents a good statistical criterion to help the user decide if a particular evaluation function is a good model for the data. If in the overall structure of most or all of the obtained fits, a tendency, other than that resembling random noise, is observed, it is
likely that the evaluation function is not a good model for the data. In XAS data analyses that exclude the EXAFS structure in the fitting, an oscillatory pattern is also observed (see for example Figure 3.23).

In addition, the scale of the residual data compared with that in the original data is another good statistical criterion. Regions with significant, relative residual intensity may be indicative of poor fitting or of an inadequate evaluation function.

In the numerical form, within the output of each fit, the goodness-of-fit is reported by means of four different statistical parameters. The simplest of such parameters is the sum of squared errors (SSE), which is defined by Equation 3.4. In essence, the closest to zero this parameter is, the better the fit.

Two additional parameters are SSR and SST. The former is defined as the sum of squares of differences between the model function evaluated at each data point using the fitted parameters and the mean of the response data set \(y\), as indicated by Equation 3.5. SST, on the other hand, corresponds to the total sum of squared deviations between each response data point and the mean of the response data set (Equation 3.6).

**Equation 3.4**  
*Sum of Squared Errors (SSE).*

\[
SSE = \sum_i d_i^2 = \sum_i (y_i - f_i)^2
\]

*Where,*

\(SSE = \text{Sum of squared errors}\)

\(d_i = \text{difference between } y_i \text{ and } f_i\)

\(y_i = i\text{-th response data point}\)

\(f_i = \text{Evaluation function at the } i\text{-th data point}\)

Since SSE depends on how intense the original data set is, the parameters SSR and SST help to define the parameter, \(r^2\), which is defined by Equation 3.7 and widely known as *coefficient of determination.* Since \(r^2\) is a "normalised" parameter, it is
sometimes more useful when comparing fits corresponding to several different, non-normalised data sets. The closer the value of this parameter is to one, the better the fit. In fact, a value of exactly $r^2=1$, will correspond to a value of exactly $SSE = 0$ and will imply that the fit and the data set are identical.

Equation 3.5  Sum of squared differences between the fit and the mean of the response data.

$$SSR = \sum_{i} (\hat{y} - f_i)^2$$

Where,

- $f_i = Evaluation\ function\ at\ the\ i-th\ data\ point\ y_i\ and\ f_i$
- $\hat{y} = Mean\ of\ the\ response\ data$

Equation 3.6  Sum of squared differences between the response data and the mean of the response data.

$$SST = \sum_{i} (\hat{y} - y_i)^2 = SSR + SSE$$

Where,

- $f_i = i-th\ response\ data\ point\ y_i\ and\ f_i$
- $\hat{y} = Mean\ of\ the\ response\ data$

Equation 3.7  Coefficient of determination.

$$r^2 = \frac{SSR}{SST} = 1 - \frac{SSE}{SST}$$

3.3.3. Reliability of fitted parameters

An additional parameter related to SSE is the mean squared error (MSE) and it constitutes the second moment (about the origin) of the error. The root of this parameter, defined by Equation 3.8 and known as the root of mean square error
(RMSE), corresponds to the standard deviation of the fit, from which uncertainties for each coefficient in the evaluation function can be estimated.

**Equation 3.8** Root of mean square error.

\[
RMSE = \sqrt{MSE} = \sqrt{\frac{SSE}{n - p}}
\]

*Where,*

- \( RMSE \) = Root of mean square error
- \( MSE \) = Mean square error
- \( SSE \) = Sum of squared errors
- \( n \) = Total number of data points
- \( p \) = Total number of coefficient parameters in evaluation function, \( f \)

The output of a fit in Blueprint XAS reports the result on this quantity. Additionally, the output also reports the value on the adjusted \( r^2 \) (Adj-\( r^2 \)) which is the normalised quantity related to RMSE and computed according to Equation 3.9.

Using these last two goodness-of-fit parameters, the user can estimate uncertainties for each parameter. However, this uncertainty is estimated as part of the output in Blueprint XAS using the obtained 'cfit' Matlab-object, which results from each fit by means of a \( t \)-student calculation in each coefficient at a given confidence interval. Importantly, even though these uncertainties are useful to report associated errors in the evaluated coefficients, these are only meaningful if a single fit is obtained. After applying the methodology described in Section 3.2, the uncertainty for each coefficient in a single fit gets systematically removed by the process of computing a large number of independent fits (large \( N \) in Equation 3.10). Therefore, the uncertainty reported throughout the different analyses included in this thesis work includes only the errors emerging from the standard deviation on the coefficient parameters among the different fits.
**Equation 3.9**  
Adjusted coefficient of determination.

\[
\text{Adj} - r^2 = 1 - \frac{\text{VAR}_E}{\text{VAR}_T} = 1 - \frac{SSE/(n-p)}{SST/(n-1)}
\]

*Where,*

\[
\text{Adj} - r^2 = \text{Adjusted coefficient of determination}
\]

\[
\text{VAR}_E = \text{Estimated variance on the errors}
\]

\[
\text{VAR}_T = \text{Estimated variance on the observations}
\]

\[
SSE = \text{Sum of squared errors}
\]

\[
n = \text{Total number of data points}
\]

\[
p = \text{Total number of coefficient parameters in evaluation function, } f
\]

**Equation 3.10**  
Propagation of uncertainty on the \( j \)-th coefficient parameter of the evaluation function, \( f \), when averaged over \( N \) fits

\[
\Delta A_{C_j}^2 = \sum_i \left( \frac{\partial A_{C_j}}{\partial C_{j,i}} \right)^2 \Delta C_{j,i}^2 = \left( \frac{\partial A_{C_j}}{\partial C_{j,i}} \right)^2 \sum_i \Delta C_{j,i}^2 = \frac{1}{N^2} \sum_i \Delta C_{j,i}^2
\]

*Where,*

\[
\Delta A_{C_j} = \text{Propagated error in the } j \text{-th coefficient averaged over } N \text{ fits}
\]

\[
C_j = j \text{-th coefficient parameter in the evaluation function, } f
\]

\[
C_{j,i} = j \text{-th coefficient parameter of } f \text{ in the } i \text{-th fit}
\]

\[
\Delta C_{j,i} = \text{Error in the } j \text{-th coefficient of } f \text{ in the } i \text{-th fit}
\]

\[
N = \text{Total number of fits}
\]

### 3.4. FEATURES AND TECHNICAL ASPECTS OF BLUEPRINT XAS

To run Blueprint XAS, Matlab 7.4.0 **R2007a** (or a more recent version) is required.

In terms of visualisation of the features in the graphical user interface (GUI), Blueprint
XAS is best viewed using wide-screen monitors with WSXGA resolution (1440x900px) or better; the minimum recommended resolution is XGA (1024x768 px). Future versions, which will include a full toolbox for XAS data pre-fitting processing, will be introduced as stand-alone executables, but given that the current suite focuses exclusively on the fitting and analysis modules, it has been left as a Matlab-based toolbox.

The major components of the fitting toolbox of Blueprint XAS are encoded in a single '.m' file (BlueprintXAS.m); a supporting '.mat' file (BlueprintXAS.mat) is also required. This latter file contains the current values for all of the objects in the GUI, as well as the data and parameters introduced by the user during the last time the toolbox was in use. Other secondary components are optional although necessary to accomplish certain tasks. Those files and accompanying documentation are currently available upon request. The basic software and supporting documentation is currently available through SourceForge.net via an open source licensing agreement (146). In the following sections, a brief overview of the main features of Blueprint XAS is provided.

### 3.4.1. Input/output and other basic features

Figure 3.3 shows a snapshot of the fitting toolbox of Blueprint XAS, as it is displayed after typing the command 'BlueprintXAS' into the command window of Matlab. To administer the space in the GUI without sacrificing quick access to the different tools and objects that are available in the program, several tab panels were created. The graphics panel is at all times visible, even though its scaling controls are located in the 'General' panel.

Data can be loaded into the program in different ways: (i) 'Calibrated' is an internal data format that will be used to load energy calibrated and averaged spectra from another pre-fitting module of Blueprint XAS (currently unavailable); (ii) 'Fit' allows for retrieval of previously fitted parameters and data as well as the GUI parameters that lead to the generation of these fits; (iii) 'Excel' allows users to load the first two columns of a Microsoft Excel ® (.xls) file; and (iv) 'Parameters' retrieves just the parameters and functions used in other sessions. This function is particularly useful if similar settings to
the data in other sessions need to be applied to the current data loaded into the program. The 'General' tab also includes the tools to run and to create batches of queued jobs, as described in Section 3.4.3.

**Figure 3.3** General panel of Blueprint XAS.

The other tab panels ('Edges', 'Background' and 'Peaks') focus on the different aspects of the overall evaluation function and the tools that help define the parameters therein. Although the default functions used in each of these tab panels are very specific to near-edge XAS data analysis, the fitting methodology is not. For example, adding an edge feature using the “Add Edge” function (see Figure 3.4) creates a new component to the fit model that corresponds to a suggested edge function. However, the fit component is completely user-editable, so that the parameters and even the functional form itself can be modified with simplicity.
For consistency, all variables within the program are labelled using mainly five identifiers: peak areas or edge intensities are labelled ‘I’ (intensity); peak or edge energies are labelled ‘O’ (position); Half-width at half maximum (hwhm) parameters are labelled W (width); the shape of a pseudo-Voigt peak or edge is labelled ‘G’ (Gaussian fraction); and branching ratios (i.e., for multi-edge spectra) are given the label ‘B.’ Table 3.2 shows the complete list of identifiers supported by Blueprint XAS. When developing the fit model (or evaluation function) for a data set, the program provides users with the ability to automatically add as many as four edges and as many as six peaks. This current limitation results from the GUI and can easily be circumvented by adding additional components directly into the evaluation function. In any case, it should be noted that data that require more than the above number of edges and peaks would be rather unusual.

The ‘Background’ panel offers specific functionality to assist in the building of a reasonable background. Initial guesses for polynomial functions fitting a particular background region are not as intuitive for the user as are the parameters in functions fitting an edge or a peak. Therefore, a pre-optimisation tool, which uses linear least
squares, is included to allow the user to rapidly define reasonable starting points for the parameters in these functions. Results from this pre-optimisation can be easily exported as initial guesses to the parameters panel by using the 'Export' function (Figure 3.5).

Table 3.2  Permitted identifiers for the setting up of functions and parameters in a fit model using Blueprint XAS

<table>
<thead>
<tr>
<th>GUI Panel</th>
<th>Permitted identifiers</th>
<th>Definition (according to default function parameters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edges, Peaks</td>
<td>I</td>
<td>Edge Intensity or peak area.</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>Energy position at edge's inflection point or at maximum height of a peak.</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>Half width at half maximum height (hwhm) of edge or peak</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>Shape of edge or peak (in Gaussian fraction)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Branching ratio (in multiple-edged problems).</td>
</tr>
<tr>
<td>Background</td>
<td>m</td>
<td>Slope in a parent linear polynomial function</td>
</tr>
<tr>
<td></td>
<td>YI</td>
<td>Y Intercept in the lowest-energy parent polynomial function</td>
</tr>
<tr>
<td></td>
<td>p</td>
<td>Quadratic coefficient in a parent quadratic polynomial function.</td>
</tr>
<tr>
<td></td>
<td>q</td>
<td>Linear coefficient in a parent quadratic polynomial function.</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>Position at the infection point of a &quot;switch-like&quot; background</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>Half width at half maximum height (hwhm) of a &quot;switch-like&quot; background.</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>Pivot energy of a &quot;handle-like&quot; background</td>
</tr>
</tbody>
</table>

To set up the background, in addition to the models that can be created by the user, two built-in weighting models are currently supported in Blueprint XAS: the handle-like (1) and the switch-like (141) (Section 2.7.3) model functions. Unlike in the cases of “Edges” and “Peaks,” a single profile for the whole background is displayed, regardless of the number of parent functions used (see Figure 3.5).

An important feature is that the coefficient parameters can be easily shared among the different components of the evaluation function, thus minimising the total number of parameters used. A particularly useful example is the sharing of the energy...
position and width between an edge and the switch-like background model (Figure 2.22).

*Figure 3.5 ‘Background’ tab panel in Blueprint XAS.*

In situations where the background differs in the pre- and post-edge regions, this serves the dual purpose of minimising parameters as well as providing a physically reasonable switch from the pre- to post-edge background functions. This feature helps the user to get a very general perspective of the problem, allowing for an insightful linking of the different parameters with relative simplicity. This is especially useful in situations where the fit model is particularly complex.

All of the settings and completed fits can be saved to name-customised files at any time using the ‘Save’ function, which is available in each of the five panels of the GUI. The ‘Exit’ function (also visible in all panels), not only closes the GUI, but also saves the current settings into the 'BlueprintXAS.mat' file (i.e., the local workspace file).
3.4.2. Background subtraction and normalisation

As of the current version (v0.2), Blueprint XAS has a post-fitting toolbox. Using this tool (Figure 3.6), background subtraction and normalisation to the data are possible using the results of a fit job. The average values of the coefficient parameters of the background from the independent fits computed within a fit job are used to retrieve the background. The 'Subtract background' function on the post-fitting GUI uses the retrieved background and subtracts it from the original data set. In a similar way, the subtraction of a fitted edge jump is also possible. The normalisation is accomplished by the use of a product that may include up to three factors. Each of these factors is set up by the user to be the average of any of the coefficient parameters obtained from the independent fits of the fit job.

Figure 3.6  Post-fitting GUI for Blueprint XAS.

The normalised and subtracted data obtained this way, along with the fit, the original data set and the average and standard deviation on the coefficient parameters in the fits, can all be exported as formatted 'txt' files. These files can be easily read in Microsoft Excel® or other spreadsheet or graphical software packages for further exploration, distribution, and publication.
3.4.3. Job options

There are several options for running jobs in Blueprint XAS. If the operational mode is set to 'Manual' (Figure 3.3), a single option is available. Under these circumstances, the 'Run' function will generate a single fit using the initial guess provided by the user. This operational mode is not significantly different from other conventional methods implemented in other existing software.

However, in the 'Auto' mode, the full methodology as described in Section 3.2 is applied. With additional options available, the user has the choice of updating the graphics in the GUI every time a new fit is successfully generated, or waiting until completion of the fits before updating the graphics. The former option may be of interest to novice users or those seeking a visual cue as to the progress of the fits, but it can dramatically increase total calculation times and it is not recommended during typical data analysis.

Given that a typical fit cycle will include a large number of independent fits (100 fits are recommended as a reasonable default (see Section 3.6.2)), the overall fit time is much longer than one might generally observe using traditional fitting software. For single edges with two to three peaks and fewer than 1,000 data points, average fitting times of one to two hours on a typical personal computer have been observed. For more complex fit models (multiple edges and five to six peaks), fit times can increase to five to eight hours. Such fitting times make use of an off-line and/or batch job type of operation more desirable. For such cases, a more efficient approach is to use the 'batch' option, which retrieves an additional working space GUI (Figure 3.7), specifically designed to set up a sequence or queue of fitting jobs. Such a queue can be run in the background with no interactive component. This approach is well suited for downloading complex fitting jobs to a high-throughput computing cluster, if available.

‡ Using a laptop computer with 2GB of RAM, with an Intel core duo processor of 1.73 GHz and a 32-bit Windows Vista operating system.
3.4.4. Statistics features

The ‘Statistics’ panel of Blueprint XAS is a crucial component of the overall methodology and represents one of the unique aspects of this data analysis toolbox. This panel allows the user to visualise relevant statistical information and explore the resultant fits. After a job has been completed, each fit, along with its individual components and its corresponding residuals, can be easily visualised using the selector in the top corner of the panel (Figure 3.8). Additionally, by selecting a fit, the summary for each fit, which includes the goodness-of-fit parameters (see Section 3.3.2) and the value of every coefficient in the model along with their confidence intervals, is displayed in the 'Details' field.

Moreover, the user can visualise the frequency distribution of fits generated in a given job according to the value of the four goodness-of-fit indicators in a logarithmic scale. Undesired fits can be filtered out by selecting a range of acceptable fit indicator values. Additionally, the user can filter a percentage of the fits to visualise only the best-ranked fits (according to their goodness of fit). Filtering by time is another useful tool, whenever fits that did not converge need to be removed. In the lower left corner of the panel, the user can explore the frequency distribution (and the deviation from an
“ideal” Gaussian distribution) for all parameters in the fits (filtered or non-filtered). In the lower right of Figure 3.8, correlation plots can be used to determine possible relationships between different parameters in the fit model.

**Figure 3.8**  'Statistics' tab panel of Blueprint XAS.

Furthermore, the 'Table' function generates a numerical summary of the fit parameters (in filtered or non-filtered sets), as shown in Figure 3.9. The time necessary to generate each fit is also displayed. In this graph, the entire non-filtered population set is displayed (solid line) in contrast with the filtered (or non-filtered) set (dots). Interestingly, fits that require significantly more time to complete than the average of fits generally correlate to non-convergent fits. A small number of such fits can easily be filtered out using the ‘TimeAvg’ option. A fit set that includes a very large number of slowly converging fits (as compared with the median fit time), however, should be considered as a warning flag of a poor fit set for which either the fit model is causing difficulties or some of the fitting parameters (e.g., MaxIter and MaxFunEvals in the general panel) should be adjusted.
3.5. INTERNAL NORMALISATION

The normalisation of the data, based on the average of fits computed and performed throughout the use of the post-fitting toolbox of Blueprint XAS (Section 3.4.2), is primarily useful to graphically compare the data obtained for several compounds. However, due to the highly interactive GUI of Blueprint XAS, an "internal normalisation" of the peak features is possible. In an internal normalisation, the intensity of the pre-edge peak is expressed as a function of the edge jump intensity directly within the evaluation function. To accomplish this task, it is necessary to edit the appropriate field in Blueprint XAS so that the corresponding function on it is multiplied by the parameter chosen to be the intensity of the normalising edge jump (Figure 3.10).

The following examples show the applicability of the methodology described in Section 3.2 by using several real examples. Throughout the analysis of these examples, the following aspects are also explored: 1) the number of fits required to
ensure statistically meaningful solutions; 2) the reproducibility and errors associated with the fitting procedure; 3) the effects of concentration in solid samples and its implications; 4) the possible propagation of errors upon background subtraction prior to the fitting procedure; and 5) the implementation of the methodology in multiple-edge XAS data.

**Figure 3.10** Internal normalisation of a Lorentzian peak, using the intensity parameter of an edge jump.

\[
L = \frac{I_2}{\pi} \times \frac{W_2}{(x - O_2)^2 + W_2^2}
\]

Where,

- \(I_2\): Intensity
- \(O_2\): Energy position
- \(W_2\): Width

\[
L = \frac{I_2 \cdot I_1}{\pi} \times \frac{W_2}{(x - O_2)^2 + W_2^2}
\]

- \(I_2\): Normalised Intensity
- \(I_1\): Intensity of Edge jump
- \(O_2\): Energy position
- \(W_2\): Width

### 3.6. DEMONSTRATIVE EXAMPLES

The first four of these issues were investigated using the XAS data collected on several samples of tetragonal (NEt₄)₂CuCl₄. The latter of these points is also addressed using the S K-edge XAS spectra of several samples of Na₂S₂O₃, a common calibrating compound used in S K-edge XAS spectroscopy. Finally, the last issue was investigated using the Ru L-edge XAS data on compound 8 (Chart 1.1).
3.6.1. Data collection and sample preparation

Tetragonal CuCl$_4^{2-}$ (i.e., with $D_{2d}$ local symmetry) has become a commonly used compound to calibrate and extract covalency on chlorine-containing metal complexes (127, 128, 147). Hence, Cl K-edge XAS data on (NEt$_4$)$_2$CuCl$_4$ represents a good reference for the applicability of the methodology introduced herein. We fitted and analyzed several data sets of solid (NEt$_4$)$_2$CuCl$_4$ collected at different times over a five-year period. The first data set corresponds to two long-range scans, in the region of from 2720 - 3150 eV, collected at beamline 6-2. The rest of the data, obtained from fourteen different samples, correspond to shorter scans (two per sample) obtained more recently at beamline 4-3, in the range of energy 2750 - 2900 eV.

The data from different samples of Na$_2$S$_2$O$_3$ were obtained in beamline 6-2 over a period of five years in the range of energy 2465 - 2485 eV. Additionally, the data for compound 8 were collected in the range of energy from 2720 - 3150 eV at beamline 6-2.

The samples prepared prior to the collection of the data were finely ground into fine powders to reduce anisotropic effects. A common vehicle to dilute the solid samples to reduce self-absorption is boron nitride (BN), a highly dense material with minimal absorption in the relevant scanning region. In the case of (NEt$_4$)$_2$CuCl$_4$, the sample used to collect the long-range scans was not diluted. However, the fourteen samples used to collect the short-range scans were diluted using different approximate proportions (in volume) of BN:(NEt$_4$)$_2$CuCl$_4$, as indicated in Table 3.4. Na$_2$S$_2$O$_3$ samples were not diluted, but prior to collecting the data, samples were somewhat ground. Finally, the sample for compound 8 used to scan the Ru L-edge XAS data was not diluted but it was finely ground.

3.6.2. How many computed fits per job?

The possibility of having multiple good solutions to a particular fitting problem makes the generation of multiple independent fits a necessity. To investigate how many fits should be generally obtained when running a job in Blueprint XAS, the two long-range scans of (NEt$_4$)$_2$CuCl$_4$ were averaged and the resulting data were fitted, using two pseudo-Voigt peaks to model the pre-edge and near-edge features, one cumulative
pseudo-Voigt function to model the edge jump and a switch-like background function to model the background (Figure 3.11). An internal normalisation of the peaks was accomplished by following the procedure described in Section 3.5.

Table 3.3 Results for fit jobs involving (a) 10, (b) 100, (c) 1,000 and (d) 10,000 independent fits in the Cl K-edge XAS long-range data set of (NEt₄)₂CuCl₄.

<table>
<thead>
<tr>
<th>Coefficient parameter</th>
<th>(a) 10 Fits</th>
<th>(b) 100 Fits</th>
<th>(c) 1,000 Fits</th>
<th>(d) 10,000 Fits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edge Intensity, I₁</td>
<td>0.246</td>
<td>0.245</td>
<td>0.245</td>
<td>0.245</td>
</tr>
<tr>
<td>Energy position (eV), O₁</td>
<td>2824.90</td>
<td>2825.29</td>
<td>2825.24</td>
<td>2825.27</td>
</tr>
<tr>
<td>Peak 1 Normalised Intensity, I₁</td>
<td>0.577</td>
<td>0.578</td>
<td>0.579</td>
<td>0.579</td>
</tr>
<tr>
<td>Energy position (eV), O₃</td>
<td>2820.16</td>
<td>&lt;0.01</td>
<td>2820.16</td>
<td>2820.16</td>
</tr>
<tr>
<td>Peak 2 Normalised Intensity, I₃</td>
<td>2.57</td>
<td>3.02</td>
<td>2.96</td>
<td>2.99</td>
</tr>
<tr>
<td>Energy Position(eV), O₃</td>
<td>2826.40</td>
<td>2826.29</td>
<td>2826.30</td>
<td>2826.29</td>
</tr>
</tbody>
</table>

A total of 10, 100, 1000 and 10000 fits were computed for the Cl K-edge XAS long-range data set on (NEt₄)₂CuCl₄, in three separate jobs. Table 3.3 lists the results obtained from these fit jobs; the average and the standard deviation of the relevant fitted parameters. Figure 3.12 shows the distribution of the start points and the fits according to their - log(SSE) value for the last three fit jobs.

As is evident from Table 3.3, the average values for the parameters corresponding to more resolved features in the spectrum, such as the pre-edge intensity (I₂) and the pre-edge energy position (O₂) are well defined when only 10 fits are obtained. However, this sample size is not large enough to estimate errors even in these parameters. The results in this table indicate that performing 100 fits give rise to better defined average values in all the parameters, as well as good estimates in their
associated errors when compared with the more time and resource demanding jobs (c) and (d).

**Figure 3.11** Evaluation function \((f)\) for the fitting of the \((\text{NEt}_4)_2\text{CuCl}_4\) long-range data set. Coefficient parameters are set as defined in Table 3.2

\[
f_e = I_1(G_1 \cdot C_G + (1 - G_1) \cdot C_L)
\]

\[
C_G = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - O_1}{W_1 / \ln 2} \right) \right]
\]

\[
C_L = \frac{1}{2} \arctan \left( \frac{x - O_1}{W_1} \right) + \frac{1}{\pi}
\]

\[
f_{p_1,p_2} = I_{2,3} \cdot I_1 \cdot (G_{2,3} \cdot F_{G_{p_1,p_2}} + (1 - G_{2,3}) \cdot L_{p_1,p_2})
\]

\[
F_{G_{p_1,p_2}} = \sqrt{\frac{\ln 2}{W_{2,3}^2 \pi}} e^{-\frac{(\ln 2)(x - O_{2,3})^2}{W_{2,3}^2}}
\]

\[
L_{p_1,p_2} = \frac{1}{\pi} \times \frac{W_{2,3}}{(x - O_{2,3})^2 + W_{2,3}^2}
\]

\[
f_b = f_1 \frac{1}{1 + e^{-(x - O_1)W_1}} + f_2 \frac{1}{1 + e^{-(O_1 - x)W_1}}
\]

\[
f_1 = m_1 \cdot x + YI
\]

\[
f_2 = p_1 \cdot (x - O_1)^2 + q_1 \cdot (x - O_1) + f_1(O_1)
\]

\[
f = f_e + f_{p_1} + f_{p_2} + f_b
\]
Furthermore, Figure 3.12 indicates that increasing the total number of fits improves the distribution profile of the start points when going from 100 to 10,000 fits; yet it does little to change the statistical results. Therefore, the amount of time spent to compute 10,000 fits in this case (8.5 days) is completely unnecessary. The results obtained from computing only 100 fits, which took only two hours in this particular case, represent an acceptable solution for this problem. We conclude from this that, in general, 100 fits should be sufficient in most cases to statistically explore the solution space of a fitting problem in XAS.

### 3.6.3. Reproducibility of fit jobs

The two scans collected for each of the fourteen (NEt₄)₂CuCl₄ samples were averaged. The resulting data sets were calibrated by adjusting to 2820.2 eV, the maximum in the pre-edge peak. The calibrated data sets are illustrated in Figure 3.13.
Figure 3.13 Calibrated data sets corresponding to the Cl K-edge XAS spectra for samples 1-14 of (NEt₄)₂CuCl₄ in (a) the entire scanned region and (b) the pre-edge region. Data sets corresponding to samples with 50% of BN are displayed as solid lines in different shades of red (darker to lighter on going from 1 to 5 in Table 3.4); data sets corresponding to samples with 75% of BN are displayed in different shades of orange plus signs (darker to lighter on going from 6-7 in Table 3.4); data sets corresponding to samples with 90% of BN are displayed as hollow circles in different shades of grey (darker to lighter on going from 8-9 in Table 3.4); and data sets corresponding to samples with more than 90% of BN are displayed as dashed lines in different shades of blue (darker to lighter on going from 10-14 in Table 3.4).

As indicated in Table 3.4, samples 1-5 were diluted with ~50% of BN, samples 6-7 with ~75% of BN, samples 8-9 with ~90% and samples 10-14 with more than 90% of
BN. It is evident from this figure that the intensity of the spectral features correlates well with the concentration of chlorine in each sample.

The evaluation function used to fit these data sets was the same in all cases, but different to the one used to fit the long-range data set. The simplified model used in this case excludes the data around the tip of the second peak (2825 - 2828.5 eV; Figure 3.14) and removes the corresponding peak function from the evaluation function, $f$ (Figure 3.15).

**Figure 3.14** Excluded data (in grey) for the fitting of Cl K-edge XAS data sets 1-14 of (NEt$_4$)$_2$CuCl$_4$.

Under these circumstances, the results from the corresponding fit jobs are inadequate to estimate the edge position, as the removal of the second peak from the model has the effect of moving the edge to lower energies. Furthermore, the edge intensity is inherently more inaccurate for these data sets, given the fact that the data scans do not go beyond 2900 eV, which otherwise would allow a better definition of the overall structure of the edge jump. In other words, the results for the edge jump parameters, although consistent among all data sets, are unimportant and not the main focus of this section. Instead, these results were very useful to compare the normalised intensity of the pre-edge feature among the different data sets, which in principle,
should all be the same according to the underlying theory in ligand K-edge spectroscopy (Section 2.4).

**Figure 3.15** Evaluation function used in the fitting of Cl K-edge XAS data sets 1-14 of (NEt₄)₂CuCl₄.

\[
f_e = I_1(G_1 \cdot C_G + (1 - G_1) \cdot C_L)
\]
\[
C_G = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - O_1}{W_1 / \ln 2} \right) \right]
\]
\[
C_L = \frac{1}{2} \arctan \left( \frac{x - O_1}{W_1} \right) + \frac{1}{\pi}
\]
\[
f_p = I_{2,3} \cdot I_1 \cdot (G_{2,3} \cdot F_G + (1 - G_{2,3}) \cdot L)
\]
\[
F_G = \sqrt{\ln 2} \cdot \frac{1}{\frac{1}{W_2^2} - \frac{1}{W_2^2}}
\]
\[
L = \frac{1}{\pi} \times \frac{W_2}{(x - O_2)^2 + W_2^2}
\]
\[
f_b = f_1 \left( 1 + e^{-\frac{(x - O_1)\ln 3}{W_1}} \right) + f_2 \left( 1 + e^{-\frac{(O_1 - x)\ln 3}{W_1}} \right)
\]
\[
f_1 = m_1 \cdot x + YI
\]
\[
f_2 = p_1 \cdot (x - O_1)^2 + q_1 \cdot (x - O_1) + f_1(O_1)
\]
\[
f = f_e + f_m + f_b
\]
For each data set, a fit job consisting of 100 fits was computed, using the same lower and upper bounds in all cases. The numerical results for the parameters of the pre-edge feature are listed in Table 3.4.

To check for reproducibility, four additional fit jobs (with 100 fits each) were obtained for samples 1 and 3 and the results for the parameters on the pre-edge feature are reported in Table 3.5. The behaviour of the variability of these results among the different fit jobs is illustrated in Figure 3.16, indicating that the methodology described herein is robust and reproducible.

Table 3.4  Results for the parameters of the pre-edge, from the fitting of Cl K-edge XAS data sets 1-14 for (NEt₄)₂CuCl₄.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalised Intensity</th>
<th>Energy position, eV</th>
<th>Width, (hwhm, eV)</th>
<th>Shape, % Gaussian</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower</td>
<td>Upper</td>
<td>Lower</td>
<td>Upper</td>
</tr>
<tr>
<td>#</td>
<td>% BN</td>
<td>Avg</td>
<td>Std</td>
<td>Avg</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>0.846</td>
<td>0.007</td>
<td>2820.20</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>0.846</td>
<td>0.010</td>
<td>2820.20</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>0.918</td>
<td>0.018</td>
<td>2820.20</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0.768</td>
<td>0.004</td>
<td>2820.20</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>0.762</td>
<td>0.007</td>
<td>2820.19</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>0.701</td>
<td>0.009</td>
<td>2820.20</td>
</tr>
<tr>
<td>7</td>
<td>75</td>
<td>0.715</td>
<td>0.045</td>
<td>2820.21</td>
</tr>
<tr>
<td>8</td>
<td>90</td>
<td>0.614</td>
<td>0.069</td>
<td>2820.20</td>
</tr>
<tr>
<td>9</td>
<td>90</td>
<td>0.630</td>
<td>0.058</td>
<td>2820.19</td>
</tr>
<tr>
<td>10</td>
<td>&gt;90</td>
<td>0.650</td>
<td>0.067</td>
<td>2820.21</td>
</tr>
<tr>
<td>11</td>
<td>&gt;90</td>
<td>0.596</td>
<td>0.074</td>
<td>2820.21</td>
</tr>
<tr>
<td>12</td>
<td>&gt;90</td>
<td>0.569</td>
<td>0.060</td>
<td>2820.22</td>
</tr>
<tr>
<td>13</td>
<td>&gt;90</td>
<td>0.702</td>
<td>0.030</td>
<td>2820.22</td>
</tr>
<tr>
<td>14</td>
<td>&gt;90</td>
<td>0.565</td>
<td>0.067</td>
<td>2820.22</td>
</tr>
</tbody>
</table>
Table 3.5  Results for the parameters on the pre-edge from additional fit jobs on Cl K-edge XAS data sets 1 and 3 of (NEt₄)₂CuCl₄.

<table>
<thead>
<tr>
<th>Sample #1</th>
<th>Normalised Intensity</th>
<th>Energy position, eV</th>
<th>Width, (hwhm, eV)</th>
<th>Shape, % Gaussian</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN 50%</td>
<td>Lower</td>
<td>Upper</td>
<td>Lower</td>
<td>Upper</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.5</td>
<td>2820</td>
<td>2821</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fit Job</th>
<th>Avg</th>
<th>Std</th>
<th>Avg</th>
<th>Std</th>
<th>Avg</th>
<th>Std</th>
<th>Avg</th>
<th>Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.846</td>
<td>0.007</td>
<td>2820.20</td>
<td>&lt;0.01</td>
<td>0.508</td>
<td>0.006</td>
<td>18.8</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>0.842</td>
<td>0.021</td>
<td>2820.20</td>
<td>&lt;0.01</td>
<td>0.507</td>
<td>0.005</td>
<td>19.0</td>
<td>3.4</td>
</tr>
<tr>
<td>3</td>
<td>0.844</td>
<td>0.005</td>
<td>2820.20</td>
<td>&lt;0.01</td>
<td>0.508</td>
<td>0.006</td>
<td>18.8</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>0.845</td>
<td>0.007</td>
<td>2820.20</td>
<td>&lt;0.01</td>
<td>0.508</td>
<td>0.007</td>
<td>18.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample #3</th>
<th>Normalised Intensity</th>
<th>Energy position, eV</th>
<th>Width, (hwhm, eV)</th>
<th>Shape, % Gaussian</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN 50%</td>
<td>Lower</td>
<td>Upper</td>
<td>Lower</td>
<td>Upper</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>1.5</td>
<td>2820</td>
<td>2821</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fit Job</th>
<th>Avg</th>
<th>Std</th>
<th>Avg</th>
<th>Std</th>
<th>Avg</th>
<th>Std</th>
<th>Avg</th>
<th>Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.914</td>
<td>0.026</td>
<td>2820.20</td>
<td>&lt;0.01</td>
<td>0.535</td>
<td>0.003</td>
<td>20.1</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.914</td>
<td>0.023</td>
<td>2820.20</td>
<td>&lt;0.01</td>
<td>0.535</td>
<td>0.003</td>
<td>20.0</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>0.915</td>
<td>0.023</td>
<td>2820.20</td>
<td>&lt;0.01</td>
<td>0.535</td>
<td>0.003</td>
<td>20.1</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.919</td>
<td>0.018</td>
<td>2820.20</td>
<td>&lt;0.01</td>
<td>0.535</td>
<td>0.003</td>
<td>20.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

3.6.4. Concentration effects

To graphically compare the results obtained from the 14 data sets on (NEt₄)₂CuCl₄, the background subtraction and normalisation of each data set are accomplished within Blueprint XAS by using the post-fitting function, as described in Section 3.5. From Figure 3.17, it is evident that by diluting the sample with BN, the intensity of the pre-edge peak decreases while the near-edge peak feature increases.

The numerical results directly obtained for the pre-edge normalised intensity indicate the same trend (Table 3.4). Along the series of data sets 1-14, a clear decrease in the normalised intensity of the pre-edge is observed (Figure 3.18). Additionally, the width seems to remain constant with a small tendency to decrease, whereas the shape of the peak becomes slightly more Gaussian.
Interestingly, as the shape becomes more Gaussian (implying a higher instrumentation error; Section 2.7.4), the uncertainty on the four coefficients increases. Specifically, in the most dilute samples (from 8 to 14), the uncertainty on the peak position is significantly increased. This is due to the fact that as the samples becomes more diluted, the influence of the background becomes more important, as suggested...
also by Figure 3.19; particularly in the case of the most dilute samples 10-14, for which
the pre-edge region of the background increases its steepness significantly.

These results imply that background subtraction and normalisation procedures
prior to fitting, especially for spectra of dilute samples, may introduce important errors
in the fit parameters.

Figure 3.17  Background subtraction and normalisation of data sets 1-14 in the range
of energy (a) 2818-2865 eV and (b) 2818-2830 eV. Colour and line style
coding are as indicated in Figure 3.13.
Figure 3.18 Variation of pre-edge parameters according to the fit results on the Cl K-edge XAS data sets 1-14 of (NEt4)2CuCl4.

The observed differences through the series are attributed to self-absorption effects (Section 2.7.5). In relatively concentrated samples, the edge jump is so intense that it gets saturated in relation to the less-intense pre-edge feature. As observed, this effect becomes less important once the sample gets significantly diluted. This has been discussed in detail previously for the case of S K-edge XAS of S8 (148). Samples with an inherently high concentration of the absorbing element (100% of Sulphur in S8; and ~30% of Cl in (NEt4)2CuCl4, by mass) are prone to important self-absorption and
anisotropic effects when the data sets come from solid samples that are concentrated and whose particle size is relatively large. In the case of \((\text{NEt}_4)_2\text{CuCl}_4\), the somewhat asymptotic behaviour of the plot for the normalised intensity at high proportions of BN (> 90%) in Figure 3.18 indicates that distortion effects are very much attenuated at this dilution level.

**Figure 3.19** Variation of background parameters according to the fit results on the Cl K-edge XAS data sets 1-14 of \((\text{NEt}_4)_2\text{CuCl}_4\).
Previous studies on the Cl K-edge XAS spectrum of tetragonal CuCl\textsubscript{4}\textsuperscript{2-} have provided an estimate on the covalency of Cu-Cl (128). In these studies, no sample dilution was performed, although a somewhat equivalent procedure was carried out to minimise possible self-absorption and anisotropic effects. This procedure was based on the analysis of the raw data obtained from several samples that were spread out over Mylar tape with increasingly thinner sample thickness. Furthermore, their fitting analysis was based on a few manually performed independent fits using traditional background subtraction and normalisation procedures. An intensity of 0.57 was found for the pre-edge feature (dotted grey line in Figure 3.18), which generally agrees with the analysis of the data discussed here within error. However, it is important to notice that the inherent uncertainty in the fitting procedure leads to a relatively large and unaccounted-for error in the reference value. The importance of this factor requires further investigation (see Chapter 7).

Additional XAS data, obtained for the six samples of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, also show important variability on the spectral features. These six samples were not diluted, but instead spread in different, random thickness and quantities over Kapton sulphur free tape. Figure 3.20 illustrates the calibrated data set for these samples (calibration was accomplished by adjusting the energy of the first peak at an energy of 2472.02 eV). The S K-edge XAS spectrum of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} exhibits a double edge jump, the first of which corresponds to the less oxidised sulphur. In addition, one pre-edge feature is observed for the first edge, whereas three peak features are observed near the second edge.

As in the case of the (NEt\textsubscript{4})\textsubscript{2}CuCl\textsubscript{4} data sets, the fitting procedure for the Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} data sets involved the computation of 100 independent fits per fit job. The evaluation function in each case is the same for all cases with a single linear polynomial function to model the background, two cumulative pseudo-Voigt functions to model the edge jumps and four pseudo-Voigt functions to model the peaks (Figure 3.21).

The lower and upper bounds were chosen to be the same for the internally-normalised peaks. The first pre-edge is internally-normalised with respect to the intensity of the first edge and the other three peak features are internally-normalised using the intensity of the second edge.
Importantly, the data sets for Na$_2$S$_2$O$_3$ were collected for calibration of sulphur K-edge XAS data relevant to other research projects in the Kennepohl group and therefore the grinding of samples was not as thorough as in the case of the data collected for (NEt$_4$)$_2$CuCl$_4$ or compound 8. These data sets are short-ranged and the definition of the second edge is not very clear. Consequently, the following discussion focuses on the normalised-intensity of the first pre-edge peak.

**Figure 3.20** Calibrated Sulphur K-edge XAS data sets 1-6 for Na$_2$S$_2$O$_3$. Concentration of Na$_2$S$_2$O$_3$, which decreases along the series 1-6, is represented by a paler grey line along this series. (b) corresponds to a rescaled version of (a) to show the contrastant intensity of the first data set compared to the rest.
Figure 3.21 Evaluation function used for fitting sulphur K-edge XAS data sets 1-6 of Na₂S₂O₃.

\[ f_{e_1,e_2} = I_{1,2}(G_1 \cdot CG_{e_1,e_2} + (1 - G_1) \cdot CL_{e_1,e_2}) \]

\[ CG_{e_1,e_2} = \frac{1}{2}\left[1 + \text{erf}\left(\frac{x - O_{1,2}}{W_1/ln2}\right)\right] \]

\[ CL_{e_1,e_2} = \frac{1}{2} \arctan\left(\frac{x - O_{1,2}}{W_1}\right) + \frac{1}{\pi} \]

\[ f_{p_1} = I_3 \cdot I_1 \cdot (G_2 \cdot FG_{p_1} + (1 - G_2) \cdot L_{p_1}) \]

\[ FG_{p_1} = \sqrt{\frac{ln2}{W_2^2 \pi}} e^{-\frac{ln2(x - O_4)^2}{W_2^2}} \]

\[ L_{p_1} = \frac{1}{\pi} \frac{W_2}{(x - O_3)^2 + W_2^2} \]

\[ f_{p_2-p_4} = I_{4-6} \cdot I_2 \cdot (G_3 \cdot FG_{p_2-p_4} + (1 - G_3) \cdot L_{p_1}) \]

\[ FG_{p_2-p_4} = \sqrt{\frac{ln2}{W_3^2 \pi}} e^{-\frac{ln2(x - O_{4-6})^2}{W_3^2}} \]

\[ L_{p_2-p_4} = \frac{1}{\pi} \frac{W_3}{(x - O_{4-6})^2 + W_3^2} \]

\[ f_b = m_1 \cdot x + YI \]

\[ f = f_{e_1} + f_{e_2} + f_{p_1} + f_{p_2} + f_{p_3} + f_{p_4} + f_b \]

Figure 3.22 shows the results for the normalised data (with respect to the first edge) that is obtained after using the post-fitting feature of Blueprint XAS. The pre-edge feature changes its normalised intensity without a clear trend and not as significantly as in the case of the pre-edge in the Cl K-edge XAS data sets. The results for the
Coefficient parameters from this feature are listed in Table 3.6. An important and more significant change is observed for the ratio between the intensities of the two edges. In principle, and since the ratio of the two chemically very distinct sulphur atoms in Na$_2$S$_2$O$_3$ is 1:1, a ratio close to one should be expected in all cases. However, self-absorption and especially anisotropic effects (for which the direction of the incident X-rays become important), may be playing a major role in the attenuation of one of the edges in relation to the other, and hence changing this ratio. Furthermore, a more significant distortion can be observed for the very intense peak features near the second edge (Figure 3.22).

Table 3.6 Results for the pre-edge parameters from the fitting of the sulphur K-edge XAS data sets 1-6 of Na$_2$S$_2$O$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalised Intensity</th>
<th>Energy position, eV</th>
<th>Width, (hwhm, eV)</th>
<th>Shape, Gaussian</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Lower</td>
<td>Upper</td>
<td>Lower</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2471.5</td>
<td>2472.5</td>
<td>0.01</td>
</tr>
<tr>
<td>Avg</td>
<td>Std</td>
<td>Avg</td>
<td>Std</td>
<td>Avg</td>
</tr>
<tr>
<td>1</td>
<td>2.565</td>
<td>0.102</td>
<td>2472.04</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>2</td>
<td>2.842</td>
<td>0.037</td>
<td>2472.00</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>3</td>
<td>2.604</td>
<td>0.004</td>
<td>2472.00</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>4</td>
<td>2.721</td>
<td>0.042</td>
<td>2472.05</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>5</td>
<td>2.202</td>
<td>0.018</td>
<td>2472.06</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>6</td>
<td>2.591</td>
<td>0.064</td>
<td>2472.00</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

The analysis of these Na$_2$S$_2$O$_3$ data sets also illustrated the advantages of fitting the background (as opposed to removing the background) to avoid the propagation of additional errors (Section 3.6.5).

3.6.5. Background removal and propagation of errors

Removing the background from the raw data prior to the fitting procedure is a common practice in the analysis of XAS data. The implications of the background subtraction in the final results of the fitting procedure are explored in the S K-edge XAS of Na$_2$S$_2$O$_3$. The results for the fit job on one of the data sets are used.
Figure 3.22 Normalised sulphur K-edge XAS data sets 1-6 for Na$_2$S$_2$O$_3$.

Figure 3.23 shows the appearance of three of the 100 fits obtained (labelled I, II and III). They represent different solutions to the same fitting problem, with a very similar residual structure. Yet, the normalised intensity of the pre-edge is significantly different, as indicated numerically in Table 3.7. The background of fits I and III is very similar and so are the remaining features. In fit II, however, the background is visually different and its impact on the intensity of the pre-edge more pronounced. This example shows the implications of subtracting a background without fitting. When doing that, the subtracted data may lose or gain significant intensity.
Table 3.7  Selected fits corresponding to the fitting of one of the S-K-edge XAS data sets of Na$_2$S$_2$O$_3$.

<table>
<thead>
<tr>
<th>Fit</th>
<th>$r^2$</th>
<th>-log(1-$r^2$)</th>
<th>Normalised intensity (Pre-edge)</th>
<th>95% Conf.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.9938</td>
<td>2.206</td>
<td>2.607</td>
<td>0.514</td>
</tr>
<tr>
<td>II</td>
<td>0.9995</td>
<td>3.320</td>
<td>2.455</td>
<td>0.199</td>
</tr>
<tr>
<td>III</td>
<td>0.9996</td>
<td>3.439</td>
<td>2.596</td>
<td>0.123</td>
</tr>
</tbody>
</table>

Figure 3.23  Detail of fits I-III, selected from a family of 100 independent fits corresponding to the fitting of one of the S K-edge XAS data sets of Na$_2$S$_2$O$_3$.

Equally important is the fact that the tails of peaks and edge jump features contribute to the background. Particularly when addressing these issues, the
advantage of using the underlying methodology encoded in Blueprint XAS is that by producing a significant number of independent fits (like I-III), the average values and the associated uncertainties in the different parameters are estimated.

### 3.6.6. Multi-edge fitting

The fitting of the Ru L_{2,3} XAS data for compound 8, using Blueprint XAS, is used 1) to demonstrate the applicability and robustness of the switch-like background model (Section 2.7.3); and 2) to show the application of the methodology when fitting multiple-edge spectra with several shared parameters.

In recent years, the exploration of L-edge XAS in second-row, transition metal complexes has grown significantly (145, 149, 150). In general, for these studies, while having a complicated background can be perceived as a disadvantage, the double edge spectrum in near $jj$-coupling conditions is actually an advantage.

Quantitative studies using the handle-like model for the background and a traditional approach to analyse the Cl K- and Ru L-edges XAS data for compounds 1, 2 (Chapter 6) and 8 (see below) suggest that the ratio between the L_{3} and L_{2} edges differs significantly from the statistical value of 2:1 (1).

The electronic structure for the final state of a second-row transition-metal complex, illustrated in Figure 2.13, is in agreement to this statistical ratio. As discussed in Section 2.5, the atomic and ligand field interactions within the 4d shell are introduced as a perturbation subsequent to the very large 2p spin-orbit coupling. The inter-electronic interactions between the multiplets in the 2p$^5$ shell and those in the 4d$^{n+1}$ are entirely neglected. Under this formalism, the structure of the L_{2} edge is essentially a smaller replica, half the size, of the structure in the L_{3} edge.

Experimentally, while the structure of the two edges in the Ru L_{2,3}-edges XAS spectrum of compound 8 remains virtually the same, the ratio seems to be somewhat different from the statistical value 2:1. Figure 3.24 illustrates this on the raw data for 8. A rough graphical manipulation of the data indicates that the proportion between the two edge jumps, and between the total intensity of the pre-edge and near edge features in the two edges, corresponds to an intensity ratio of $\approx$1.7. This is not
exclusive of compound 8, but rather a general observation for second-row, transition-metal complexes (Chapter 6), (151).

Figure 3.24 Rough graphical manipulation of the raw Ru L_{2,3} XAS spectra for compound 8. The energy scale is relative to the maximum of the pre-edge feature in L_3 (around 2842 eV) and to the maximum of the pre-edge feature in L_2 (~2842+128.7 eV). The intensity of the L_2 edge is rescaled using a factor of 1.7

The formulation of an evaluation function for the fitting of this and similar data becomes simpler when considering these observations. A unique parameter that relates the intensity of the two edge jump functions as well as the intensity of the two clusters of peaks in the two edges can be used. In Blueprint XAS, the implementation of models that makes use of global and shared parameters is more obvious; a clearer and more general perspective of a particular fitting problem comes to light naturally under the program's design. Figure 3.25 shows an initial formulation of the evaluation function as implemented in Blueprint XAS. Within this model, the use of lower and upper bounds for the branching ratio B_1 is almost redundant. The fact that B_1 is part of several of the features in the model (f_0, f_{p1-f_{p3}}) imposes important constraints that ultimately facilitates the overall fitting procedure.
Figure 3.25 Evaluation function for the fitting of the Ru L_{2,3}-edges XAS spectrum of compound 8.

![Graph](image)

\[
 f_b = \frac{f_1}{1 + e^{(x-O_1)/W_1}} + \frac{f_2}{(1 + e^{(O_1-x)/W_1})(1 + e^{(x-O_2)/W_1})} + \frac{f_3}{1 + e^{(O_2-x)/W_1}}
\]

\[
 f_1 = m_1 x + Y1, \quad f_2 = m_2 (x - O_1) + f_1(O_1), \quad f_3 = m_3 (x - O_2) + f_2(O_2)
\]

\[
 f_e = B_1 \cdot I_1 \left[ G_1 \cdot \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - O_1}{W_1/\ln 2} \right) \right] + (1 - G_1) \cdot \left( \frac{1}{2} \arctan \left( \frac{x - O_1}{W_1} \right) + \frac{1}{\pi} \right) \right]
\]

\[
 + I_1 \left[ G_1 \cdot \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - O_2}{W_1/\ln 2} \right) \right] + (1 - G_1) \cdot \left( \frac{1}{2} \arctan \left( \frac{x - O_2}{W_1} \right) + \frac{1}{\pi} \right) \right]
\]

\[
 f_{p2} = B_1 \cdot I_2 \cdot I_1 \left[ G_2 \cdot \sqrt{\frac{\ln 2}{W_3^2 \pi}} e^{-\frac{(x-O_1)^2}{W_3^2}} + \frac{(1 - G_2)}{\pi} \cdot \frac{W_3}{(x - O_4)^2 + W_3^2} \right]
\]

\[
 + I_2 \cdot I_1 \left[ G_2 \cdot \sqrt{\frac{\ln 2}{W_3^2 \pi}} e^{-\frac{(x-O_2)^2}{W_3^2}} + \frac{(1 - G_2)}{\pi} \cdot \frac{W_3}{(x - O_5)^2 + W_3^2} \right]
\]

\[
 f_{p1,p3} = B_1 \cdot B_{2,3} \cdot I_2 \cdot I_1 \left[ G_2 \cdot \sqrt{\frac{\ln 2}{W_3^2 \pi}} e^{-\frac{(x-O_6,7-O_4)^2}{W_3^2}} + \frac{(1 - G_2)}{\pi} \cdot \frac{W_3}{(x - O_{6,7} - O_4)^2 + W_3^2} \right]
\]

\[
 + B_{2,3} \cdot I_2 \cdot I_1 \left[ G_2 \cdot \sqrt{\frac{ln 2}{W_3^2 \pi}} e^{-\frac{(x-O_8,9-O_5)^2}{W_3^2}} + \frac{(1 - G_2)}{\pi} \cdot \frac{W_3}{(x - O_{8,9} - O_5)^2 + W_3^2} \right]
\]

Furthermore, since the peak features in $f_{p1}$ and $f_{p3}$ are not very intense, compared with the dominant $f_{p2}$, the intensities of these two functions are set as a fraction (B_2 and B_3, respectively) of the intensity of $f_{p2}$. For the same reason, the energy positions of the features in these two functions were set as relative to the position of the features in $f_{p2}$. 

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The shape \((G_2)\) and the hwhm-width \((W_3)\) parameters were set to be the same in all of the three "double" peak functions. This last assumption may not always be suitable in the fitting of other, more complicated spectra, although it can be generally attempted.

**Figure 3.26** Energy correlation between the position of the edges and the peak features in \(L_{2,3}\)-edges XAS under nearly \(jj\)-coupling conditions, for which the dominant interaction is the \(2p\) spin-orbit coupling. The remaining interactions can be considered as perturbations of the same magnitude for each edge.

The model in Figure 3.25 can be further simplified by taking into consideration that the energy separation between the inflection points of the two edges may be the same as the separation of *equivalent* peak features between the two edges, as shown in Figure 3.26. In general, this is a very likely simplification to the problem under near \(jj\)-
coupling conditions in which the atomic, the ligand field and the bonding perturbations that occur in one edge or the other are of the same magnitude. As suggested by Figure 3.24, this should be the case in compound 8. Based on these additional considerations, the evaluation function used in the fitting of the Ru L_{2,3}-edges XAS spectrum of compound 8, was simplified as shown in Figure 3.27. In this model, the equivalent peaks in each function were linked using the energy splitting (W_2) between the two edge jumps (removing unnecessary energy position parameters such as O_2, O_5, O_8 and O_9). Using this last evaluation function, three fit jobs with 100 fits each were computed. The results, for relevant parameters, are listed in Table 3.8.

<table>
<thead>
<tr>
<th>Coefficient parameter</th>
<th>Bound</th>
<th>Fit Job #1</th>
<th>Fit Job #2</th>
<th>Fit Job #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Branching ratio, B_1</td>
<td>1.3</td>
<td>2.5</td>
<td>1.73</td>
<td>1.73</td>
</tr>
<tr>
<td>W_2</td>
<td>128</td>
<td>130</td>
<td>128.7</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>L_3 Edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inflection point, O_1</td>
<td>2837</td>
<td>2843</td>
<td>2841.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Shape, G_1</td>
<td>0</td>
<td>100</td>
<td>33.0</td>
<td>20.4</td>
</tr>
<tr>
<td>Width, W_1</td>
<td>0.1</td>
<td>3</td>
<td>1.79</td>
<td>0.61</td>
</tr>
<tr>
<td>Peaks</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shape, G_2</td>
<td>0</td>
<td>100</td>
<td>18.4</td>
<td>8.8</td>
</tr>
<tr>
<td>Width, W_3</td>
<td>0.05</td>
<td>3</td>
<td>1.28</td>
<td>0.10</td>
</tr>
<tr>
<td>f_p1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative position, O_6</td>
<td>-2.5</td>
<td>-0.5</td>
<td>-1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Relative intensity, B_2</td>
<td>0</td>
<td>1</td>
<td>0.236</td>
<td>0.206</td>
</tr>
<tr>
<td>f_p2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Position, O_4</td>
<td>2841</td>
<td>2843</td>
<td>2842.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Normalised intensity, l_2</td>
<td>2</td>
<td>20</td>
<td>12.7</td>
<td>1.9</td>
</tr>
<tr>
<td>f_p3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative position, O_7</td>
<td>0.5</td>
<td>3</td>
<td>1.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Relative intensity, B_3</td>
<td>0</td>
<td>1</td>
<td>0.185</td>
<td>0.196</td>
</tr>
</tbody>
</table>
Figure 3.27 Simplified evaluation function for the fitting of the Ru L_{2,3}-edges XAS spectrum of compound 8. The splitting, due to the 2p spin-orbit coupling, denoted here as W_2 is used to constrain not only the inflection points of the two edges, but also the position of equivalent peaks in these two edges.

\[
\begin{align*}
\text{Energy, eV} & \\
2750 & 2800 & 2850 & 2900 & 2950 & 3000 & 3050 & 3100 & 3150 \\
\end{align*}
\]

\[
f_b = \frac{f_1}{1 + e^{(x-\Omega_1)/W_1}} + \frac{f_2}{(1 + e^{(\Omega_1-x)/W_1})} + \frac{f_3}{1 + e^{(\Omega_1+W_2-x)/W_1}}
\]

\[
f_1 = m_1 x + Y I, \quad f_2 = m_2 (x - \Omega_1) + f_1(\Omega_1), \quad f_3 = m_3 (x - \Omega_1 - W_2) + f_2(\Omega_1 + W_2)
\]

\[
f_e = B_1 \cdot I_1 \left[ G_1 \cdot \left( 1 + \text{erf} \left( \frac{x - \Omega_1}{W_1/\ln 2} \right) \right) + (1 - G_1) \cdot \left( \frac{1}{2} \arctan \left( \frac{x - \Omega_1}{W_1} \right) + \frac{1}{\pi} \right) \right] \\
+ I_1 \left[ G_1 \cdot \left( 1 + \text{erf} \left( \frac{x - \Omega_1 - W_2}{W_1/\ln 2} \right) \right) + (1 - G_1) \cdot \left( \frac{1}{2} \arctan \left( \frac{x - \Omega_1 - W_2}{W_1} \right) + \frac{1}{\pi} \right) \right]
\]

\[
f_{p2} = B_1 \cdot I_2 \cdot I_1 \left[ G_2 \cdot \sqrt{\frac{\ln 2}{W_3^3 \pi}} e^{-\ln^2(x-\Omega_1)/W_3^2} + \frac{(1 - G_2)}{\pi} \cdot \frac{W_3}{(x - \Omega_4)^2 + W_3^2} \right] \\
+ I_2 \cdot I_1 \left[ G_2 \cdot \sqrt{\frac{\ln 2}{W_3^3 \pi}} e^{-\ln^2(x-\Omega_2)/W_3^2} + \frac{(1 - G_2)}{\pi} \cdot \frac{W_3}{(x - \Omega_4 - W_2)^2 + W_3^2} \right]
\]

\[
f_{p1,p3} = B_1 \cdot B_{2,3} \cdot I_2 \cdot I_1 \left[ G_2 \cdot \sqrt{\frac{\ln 2}{W_3^3 \pi}} e^{-\ln^2(x-\Omega_{6,7}-\Omega_4)/W_3^2} + \frac{(1 - G_2)}{\pi} \cdot \frac{W_3}{(x - \Omega_{6,7} - \Omega_4)^2 + W_3^2} \right] \\
+ B_{2,3} \cdot I_2 \cdot I_1 \left[ G_2 \cdot \sqrt{\frac{\ln 2}{W_3^3 \pi}} e^{-\ln^2(x-\Omega_{6,7}-W_2-\Omega_4)/W_3^2} + \frac{(1 - G_2)}{\pi} \cdot \frac{W_3}{(x - \Omega_{6,7} - W_2 - \Omega_4)^2 + W_3^2} \right]
\]
The variability of $W_2$ is minimal and practically the same as in ruthenium metal ($\sim 129 \text{ eV}$) (112). This implies that possible interactions of the valence shell with the 2p core hole in the ruthenium metal, or in other words, that the spin-orbit coupling for the 2p-shell of ruthenium (II) in compound 8, is essentially that of ruthenium metal. Conversely, a large variability is observed for the parameters of the three peak
functions in the fits of the three jobs, particularly their intensity, as evidenced by the results in Table 3.8 and Figure 3.28. In situations like this, in which a pre-edge or near-edge feature is not well-resolved, the spectrum itself is not good enough to give a simple solution based on a single or even a few independent fits.

From previous studies on the same data set (1), using another background model in combination with more traditional approaches, the ratio exclusively between the intensities of the two edges was reported to be 1.74 (See Chapter 6). Herein, the value for this parameter, which was also used to correlate the intensities of equivalent peak features in the two edges, is in close agreement with $B_1 = 1.73 \pm 0.05$.

The same methodology discussed in this section, can be easily employed to explore more complicated cases, allowing for a robust and methodical approach to identify whether meaningful chemical information may be effectively extracted from a specific data set. For instance, in the overlap between Ru L$_{2,3}$-edges and Cl K-edges as a cause of concern for the investigation of ruthenium-based olefin metathesis catalysts (1, 2), as well as in ruthenium-containing anticancer targets (145). Furthermore, the model can also be used to check for possible distortions in the data, in the sense that if the evaluation function does not seem to fit properly a particular set, it might very well be due to the presence of important distortions in one or more features, or else due to the presence of impurities.
CHAPTER 4: COMPUTATIONAL METHODS

The increase in the capacity and the widespread use of computers has stimulated, in the last two decades, the development of new computational methods in chemistry. In transition metal and organometallic chemistry, density functional theory (DFT) methods, for example, are now used routinely to provide rationalisations on the observed reactivity of newly developed or long-intriguing compounds. In the case of ruthenium-based carbene complexes, several DFT-based studies (29, 30, 89, 90, 99, 152, 153) have provided important clues about the details of the mechanism and to the structure of these species.

In this thesis work, DFT methods were used with two main purposes: first, as an important aid in the interpretation of some of the XAS data analysed, and second, as a way to calibrate and back-up the obtained DFT results with experimental evidence, given the fact that quite often, there is an important bias in the community to rely on DFT methods alone to explain experimental observations. In Sections 4.1 and 4.2, a brief introduction and description of the DFT methods and parameters used is provided.

In addition to DFT, computer simulations based on a ligand-field and VBCI formalism were implemented in a new computer program in order to analyse XAS data, as discussed in Section 6.1.4. In Section 4.3, a detailed description of the underlying theory behind these simulations is provided.

4.1. GENERAL CONSIDERATIONS ON DFT METHODS

The basis for DFT relies on the proof that the ground state energy of the electrons in a given molecule is determined by the total electron density ($\rho$) of the system (154). The DFT calculations presented in this thesis were performed using the Amsterdam Density Functional (ADF) Software Package 2007.01 (155-157).

Modern DFT methods implemented in ADF are based on the Kohn-Sham theory (158), which essentially makes use of initial guesses on the Kohn-Sham (KS) orbitals to calculate the total electron density ($\rho$), which in turn is used to calculate the kinetic
(T[\rho]), nuclear-electronic (V_{ne}[\rho]), inter-electronic (J[\rho]) and exchange-correlation (E_{xc}[\rho]) terms in the KS operator, \( K \) (analogous to the Hamiltonian operator in the Schrödinger equation). The initial calculation of the total density from a basis set of orbitals is an approximation of the exact density and therefore, the solution of the Kohn-Sham equations involves the calculation of a new set of KS orbitals until self consistency is reached (Figure 4.1).

**Figure 4.1** Methodology based on the Kohn-Sham theory and implemented in modern computer DFT packages.

In this description, the terms of the KS operator (\( K \)) are called functionals simply because they depend on a function (the electron density, \( \rho \)). Moreover, the initial approximation of the density relies on the assumption of non-interacting electrons. As a result, the exchange-correlation functional is introduced as part of this Kohn-Sham
operator to account for the corrections to the kinetic and inter-electronic terms as well as for the exchange term. This exchange-correlation term is a uniquely defined functional, valid for all systems. However, an explicit form for it remains elusive and semi-empirical developed functionals, tailored for specific systems, are used instead.

The *level of theory* used in these DFT calculations is primarily determined by the choice in the exchange-correlation functional and by the basis set. The *core potential approximation* used, or more specifically (if using ADF) the integration level, are some of the additional considerations which help define the level of theory used. See Sections 4.1.1-4.1.3 for additional details on this.

### 4.1.1. Exchange-correlation functionals

A combination of theory and empirical methods, for which several parameters are fit and calibrated to a particular system or set of similar systems, is used to develop exchange-correlation functionals. Based on first principles, the local density approximation (LDA) is the default functional. It makes use of the local density of the electron and assumes homogeneity of this density in the entire space.

Since LDA is only an approximation, additional corrections, based on the first derivative (gradient-corrected methods) or higher-order derivatives on the density, are often employed. Based on several studies that have given accurate results on both main group (159) and transition metal (160) systems, the Vosko-Wilk-Nusair local density approximation (161) in conjunction with the gradient-corrected functional model for exchange by Becke and the gradient-corrected model for correlation by Perdew (BP86) (162-164), as implemented in ADF, were used to build the models for all DFT calculations described in this thesis work.

### 4.1.2. Basis sets

The use of hydrogen-type orbitals as the basis set to model the orbitals in the atoms of a given system is prohibitive due to the computational resources that would be required. Instead, making use of the *expansion theorem*, two different types of functions are employed.
According to the expansion theorem, any given continuous function of a set of variables can be described in terms of a linear combination of a complete set of functions with the same set of variables. Perhaps the most popular and widely used example of this theorem is the Fourier series, for which a linear combination using a complete set of sine or cosine functions is employed to expand a given function.

Two different types of functions are used to express the form of the KS orbitals (Equation 4.1). In the first case, a linear combination of Gaussian-type orbital functions (GTO) is used. This is the case when using GAUSSIAN, a commonly used computational package for DFT. Alternatively, a linear combination of Slater-type orbital functions (STO) (165) can be used. These two types of functions both share with the hydrogen-type the spherical harmonics component to model the angular part of the function, but they both use a simplified version of the radial component.

Even though the integrals that involve Gaussian-type orbitals have an analytical solution (as opposed to STOs), ADF uses linear combinations of STOs to model the KS orbitals. In any case, the use of a linear combination of one or another set to model such orbitals is never complete in the sense that the linear combination in Equation 4.1 is truncated at a low number of them. The advantage of using STOs is that a smaller number of them is required to model KS orbitals, up to a certain level of accuracy, when comparing to the number of GTOs that will be required in an equivalent calculation. The disadvantage, however, is that the integrations required to evaluate the matrices involved in the computation of the KS equations can only be carried out numerically with a given integration accuracy. In the calculations described in this thesis work, a default value of $10^{-6}$ for the integration accuracy was used.

Moreover, as stated before, the number of STOs to model each KS orbital in the system additionally defines the level of theory used in the calculations. For example, if a single STO is used, the type of calculation is classified as a single-zeta calculation. Increasing the number of STOs to model each orbital increases not only the accuracy of the calculation but also the required computational resources. As shown in Chapters 5 and 6, a triple-zeta with additional polarisation (TZP) basis set was good enough in most of the calculations relevant to this thesis.
Equation 4.1 Atomic orbital wave function expanded as a linear combination of Slater-type or Gaussian-type orbital basis sets.

\[
\phi_j = \sum_{i=1}^{\infty} a_{ji} \cdot \chi_{STO,i} = \sum_{i=1}^{\infty} a_{ji} \cdot N_i Y_{\ell_i,m_i} r^{n_i-1}(\theta, \varphi) e^{-\zeta_i r}, \quad \text{(Slater-type)}
\]

\[
= \sum_{i=1}^{\infty} b_{ji} \cdot \chi_{GTO,i} = \sum_{i=1}^{\infty} b_{ji} \cdot N_i Y_{\ell_i,m_i} (\theta, \varphi) r^{2n_i-2-\ell_i} e^{-\zeta_i r^2}, \quad \text{(Gaussian-type)}
\]

Where,

\[
\phi_j = j\text{-th KS orbital expressed as a linear combination of functions}
\]

\[
a_{ji}, b_{ji} = \text{Weighting coefficients}
\]

\[
= \langle \phi_j | \chi_{STO,i} \rangle, \langle \phi_j | \chi_{GTO,i} \rangle
\]

\[
\chi_{STO} = \text{Slater-type orbital}
\]

\[
\chi_{GTO} = \text{Gaussian-type orbital}
\]

\[
Y_{\ell,m}(\theta, \varphi) = \text{Spherical harmonic}
\]

\[
r = \text{distance of the electron from the atomic nucleus}
\]

\[
n, \ell, m = \text{quantum numbers}
\]

\[
\zeta = \text{effective nuclear charge}
\]

\[
N = \text{Normalisation constant}
\]

When using a TZP basis set, a total of four STOs are used to model each KS orbital. The first three share the same value on the angular momentum quantum number, \( \ell \), with the one on the corresponding KS orbital. The additional one contains an STO in which the value of \( \ell \) has been increased by one. This "polarised" STO provides additional "flexibility" to the KS orbital in order to accommodate electronic density in additional directions.
4.1.3. Effective core potentials

The use of a TZP basis set to express each orbital in a complex system significantly increases computational resources. Furthermore, systems that involve heavier elements contain a large number of core electrons that are not of great significance chemically. In addition, relativistic effects start to play a major role when dealing with such elements. Ruthenium complexes lie in this category. Hence, to simplify the problem in such cases, an effective core potential (ECP) model was implemented (166). Within this model, the core electrons in a given system are represented by an ECP function, which essentially "freezes" the core electrons up to a given shell and treats them as if they were part of a larger nucleus.

In most of the calculations discussed in this thesis work, no ECP was used for any of the elements involved, except for ruthenium. For this element, the \([\text{Ar}]^{18}\text{3d}^{10}\) core electrons were treated by the frozen core approximation.

4.2. TYPES OF DFT CALCULATIONS RELEVANT TO THIS THESIS

4.2.1. Geometry optimisation

One of the types of DFT calculations performed on compounds in Chart 1.1 was the geometry optimisation. Where available, the crystal structure of the compound under investigation was taken as a reference to optimise the geometry, which technically corresponds to the geometry in the gas phase given the fact that no lattice interactions were included (a single molecule was considered). In the cases where there was a crystal structure available, the optimised geometry was in very close agreement, as detailed in Chapter 5. Therefore, it was assumed that the optimised geometry for the rest of the compounds was somewhat accurate.

The objective function \(F\), Equation 3.2) in a DFT geometry optimisation differs from that of a curve fitting non-linear least-squares optimisation in the sense that is not the sum of squared differences that is being minimised. Instead, the total electronic energy, as a function of the coordinates of all the nuclei in the molecule, is optimised. Therefore, there is the risk of having a negative definite Hessian matrix. Similarly to curve fitting optimisations in Blueprint XAS, a Newton-step based algorithm is used by
ADF to optimise the geometry (167, 168). This optimisation is also based on a quadratic approximation of the objective function (F), and the estimation of an initial value of the Hessian matrix is based on a force-field approximation incorporated in the program. The Hessian is subsequently improved at each step of the optimisation using, for example, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme (169-172) (the default in ADF), which contains a bias to keep the Hessian matrix positive-definite, as it is required for a fast convergence.

An important choice prior to a geometry optimisation is which kind of coordinates to use. In ADF, three different frameworks are available: Cartesian (x, y, z), internal or delocalized internal coordinates (173, 174). Under the Cartesian framework, the objective function F (Equation 3.2) is optimised with respect to 3N coordinates (three for each atom), none of which is meaningful chemically. Geometry optimisations performed using this kind of framework are slower because the optimisation may undergo a direction that is not related to any of the chemically relevant directions at a given iteration step. A faster approach is the use of internal coordinates (175), which makes use of bond distances, bond angles and dihedral angles (defined in Figure 4.2).

**Figure 4.2** Internal coordinates: bond distance, $r$; bond angle, $\theta$; and dihedral angle, $\phi$.

With this framework, only 3N-6 coordinates are used, eliminating those whose displacement would formally involve translation and rotation of the whole molecule. Additionally, with internal coordinates the gradient points into directions that depend on combinations of more chemically meaningful coordinates, whereas the Hessian matrix elements provide a direct measure proportional to force constants in addition to
information regarding the coupling of the different coordinates (or modes of vibration) in the system. More recently implemented in ADF are the delocalized internal coordinates that group coupling coordinates to further reduce redundant movements upon the optimisation process and that ultimately reduce computation times.

The geometry optimisations in this thesis work were all performed using delocalized coordinates.

**Geometry alignment and the index of alikeness**

Trying to align the DFT-optimised geometry of a given compound with its crystal structure can be a very tiresome task. A Matlab-based software under development makes use of a parameter, termed herein as "similarity index" to facilitate this process.

The similarity index ($I_S$) between two geometries (A and B) is defined as the projection of a set of Cartesian coordinates in one of the geometries, into the set of Cartesian coordinates of the other (Equation 4.2). When the atoms of one of these geometries completely superimpose the atoms of the other geometry, a value of $I_S = 1$ is obtained.

For any two given geometries, the Matlab-based program aligns the structures by the systematic optimisation of the corresponding $I_S$ value, using the following algorithm in three steps (see also Figure 4.3):

**Step 1**: The same atom in each geometry is set as the origin;

**Step 2**: The same bond in each geometry is set as the z-axis;

**Step 3**: One of the structures is rotated around the z-axis a full 360 degrees with respect to the other. At each increment (defined by the user), the value of $I_S$ is evaluated. Steps 2 and 3 may be repeated to explore the alignment around other different bonds connected to the origin atom.

The alignment with the higher value of $I_S$ is chosen by the program as the result of the optimisation and it saves the obtained coordinates under the optimised alignment conditions of both geometries as separate 'xyz' files. The two sets of optimised
coordinates can then be used to make a visual comparison of the two geometries, whereas the corresponding value of $I_S$ is the numerical equivalent.

**Equation 4.2**  
Similarity Index between two geometries $A$ and $B$.

$$I_S = \frac{1}{N} \sum_{i=1}^{N} \frac{R_{(A_i,B_i),<}}{R_{(A_i,B_i),>} \left( \sum_{j=1}^{3} a_{i,j} b_{i,j} \right)}$$

Where,

- $I_S = \text{Similarity index}$
- $A_i = \text{Vector representation for the coordinates of the } i\text{-th atom in geometry } A, \text{ with norm } R_{A_i}$
- $B_i = \text{Vector representation for the coordinates of the } i\text{-th atom in geometry } B, \text{ with norm } R_{B_i}$
- $a_{i,j} = x (j = 1), y (j = 2), \text{ or } z (j = 3) \text{ component of the vector of coordinates for the } i\text{-th atom in geometry } A$
- $b_{i,j} = x (j = 1), y (j = 2), \text{ or } z (j = 3) \text{ component of the vector of coordinates for the } i\text{-th atom in geometry } B$
- $R_{(A_i,B_i),<} = \text{The minor between the norm of vector of coordinates } A_i \text{ and the norm of vector of coordinates } B_i$
- $R_{(A_i,B_i),>} = \text{The major between the norm of vector of coordinates } A_i \text{ and the norm of vector of coordinates } B_i$
- $N = \text{Total number of atoms in geometries } A \text{ or } B$

To illustrate the application of the optimisation of $I_S$ parameter when aligning any two geometries, the crystal structure of tetragonal CuCl$_4^{2-}$ (176) was optimised in ADF 2007.01 using the level theory described previously in Sections 4.1.1-4.1.3. The results of this geometry optimisation are shown in Figure 4.4.
Then, the crystal structure of CuCl$_4^{2-}$ (Figure 4.4b) is aligned with this DFT-optimised geometry by setting the copper atom as the origin in both cases. In the process, a full 360-degrees exploration around one of the Cu-Cl bonds in the DFT-optimised geometry gave rise to a maximum value of $I_S = 0.9539$.

**Figure 4.3** Algorithm implemented in a Matlab-based program used to optimise the $I_S$ value between any two geometries A and B. The optimisation around a single X-Y bond is displayed.

![Algorithm diagram](image)

Figure 4.5 illustrates the superimposed geometries and the corresponding $I_S$ values at various rotation angles for the DFT-optimised geometry around the z-axis. In this example, the copper was selected as the origin for the alignment, but in principle, any other atom could have been used for this purpose. Furthermore, the rotation around a single Cu-Cl bond was explored here, but for a higher level of rigour, the search for a better $I_S$ could have been extended to other Cu-Cl bonds. Therefore, a full
optimisation of $I_S$, would involve the repetition of this procedure by exploring the alignment centered around every atom and by exploring the z-axis rotation around different combinations of equivalent bonds between the two geometries.

**Figure 4.4** Internal coordinates for (a) geometry of CuCl$_4^{2-}$ moiety in crystal structure of (NEt$_4$)$_2$CuCl$_4$ in comparison with (b) the corresponding internal coordinates in its DFT-optimised geometry

![Figure 4.4](image)

**Internal coordinates of (a) Crystal structure**

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond Angles (deg)</th>
<th>Dihedral angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cl$_1$</td>
<td>2.2302</td>
<td>Cl$_1$-Cu-Cl$_2$</td>
</tr>
<tr>
<td>Cu-Cl$_2$</td>
<td>2.2302</td>
<td>Cl$_1$-Cu-Cl$_3$</td>
</tr>
<tr>
<td>Cu-Cl$_3$</td>
<td>2.2302</td>
<td>Cl$_1$-Cl$_4$</td>
</tr>
<tr>
<td>Cu-Cl$_4$</td>
<td>2.2302</td>
<td></td>
</tr>
</tbody>
</table>

**Internal coordinates of (b) DFT-optimised geometry**

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond Angles (deg)</th>
<th>Dihedral angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cl$_1$</td>
<td>2.3564</td>
<td>Cl$_1$-Cu-Cl$_2$</td>
</tr>
<tr>
<td>Cu-Cl$_2$</td>
<td>2.3565</td>
<td>Cl$_1$-Cu-Cl$_3$</td>
</tr>
<tr>
<td>Cu-Cl$_3$</td>
<td>2.3564</td>
<td>Cl$_1$-Cu-Cl$_4$</td>
</tr>
<tr>
<td>Cu-Cl$_4$</td>
<td>2.3565</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry considerations may also be taken into account in the evaluation of $I_S$. This is not the case for the example given in Figure 4.5: at 120 or 240 degrees, for example, rather than considering the better superposition between "adjacent" chlorine...
atoms, the projection of the coordinates $A_i B_i$ (Equation 4.2) is evaluated between the originally "equivalent" chlorine atoms in the two geometries.

**Figure 4.5** Alignment of the crystal structure of $\text{CuCl}_4^{2-}$ (dark grey) with its DFT-optimised geometry (light grey). Superimposed geometries are shown in the xy-plane for various rotation angles around the z-axis for the DFT-optimised geometry in relation to its fixed crystal structure.

While these symmetry considerations may be important in highly symmetric compounds such as $\text{CuCl}_4^{2-}$, they are not important in the cases introduced in Chapter
5. Therefore, no further discussion of these is needed here, other than to comment that future-related work will focus on implementing tools in the under-development Matlab program to effectively process such cases.

### 4.2.2. Ground state calculations

Ground state DFT calculations, based on the methodology shown in Figure 4.1, were performed in ADF from previously optimised or from crystal structure geometries by using the level of theory described in Sections 4.1.1-4.1.3.

In this type of calculation, the diagonalisation of the Kohn-Sham matrix (based on the KS equations) gives rise to the energy of the different molecular orbitals (eigenvalues) and the expansion coefficients (as eigenvectors) of the different basis set functions that constitute each of these molecular orbitals (Equation 4.3).

#### Equation 4.3

Matrix method used to solve the KS equations in a ground-state DFT calculation or at every iterative point on a geometry optimisation.

\[
C^T \cdot K \cdot C = S \cdot E
\]

With,

\[
K_{ij} = \langle \chi_i | \hat{K} | \chi_j \rangle \quad \text{and} \quad S = \langle \chi_i | \chi_j \rangle
\]

Where,

- \( C = n \times n \) matrix with expansion coefficients in the \( n \) columns corresponding to \( n \) KS orbitals
- \( C^T = \) Transpose of \( C \)
- \( K = \) Kohn-Sham matrix, with elements \( K_{ij} \) evaluated from basis set functions \( \chi_i \) and \( \chi_j \)
- \( E = \) Diagonal matrix with eigenvalues, \( \epsilon_i \)
- \( S = \) Overlapping matrix
  - \( = 0, \) (if basis set is orthonormal)
The expansion coefficients in matrix C, along with the overlap matrix S (Equation 4.3), are used through a Mulliken Population Analysis (MPA) to distribute the electrons as atomic contributions into the different molecular orbitals, as described elsewhere (177). The result from this procedure is included in the output file of an ADF ground-state calculation. The gross charge on each atom, based on this MPA electron distribution, is calculated and also included in the output file.

In addition to the atomic charges based on the MPA procedure and the corresponding atomic contributions to the molecular orbitals, the output of a ground-state calculation in ADF provides the energy of each orbital (eigenvalues in Equation 4.3), the occupation number and the atomic charges by means of other useful methods: Voronoi, Hirshfield (178) and Multipole analysis (179).

In Chapters 5 and 6, the output of the DFT ground state calculation for compounds 1-5 is used to help in the rationalisation of XAS data.

4.2.3. Time-dependent DFT and XAS

XAS is not a ground-state-based technique. Therefore, a ground-state DFT calculation is usually not suitable for interpreting XAS data. As stated in Section 2.4.3, electronic relaxation effects may play a major role in XAS, especially when transitions to different kinds of orbitals are involved. In such cases, empty ligand-based molecular orbitals may be affected differently than the metal-based orbitals upon the formation of a core hole in XAS, depending also on the edge under exploration.

Time dependent DFT calculations provide additional clues to the dynamic processes involved once the electron is being promoted to empty molecular orbitals of a given compound. Therefore, based on recommendations from previous studies (180), the LDA functional with gradient corrections from Becke and Perdew was used to obtain the line-strengths of relevant Cl K-edge XAS data (see Chapter 6). In these calculations, the level of theory described in Sections 4.1.1-4.1.3 was used. Subsequent simulations were obtained for the obtained line strengths and fitted using Blueprint XAS, as described in Section 4.4.
4.2.4. Electronic Relaxation and $\Delta$SCF DFT

In some cases where there was an apparent and important discrepancy between the computed spectra and the experimental XAS data (Chapter 6), an alternative DFT method was also used to explore possible relaxation effects that are not inherently addressed in a time-dependent DFT calculation.

In this method, known as the Slater transition state $\Delta$SCF approach (181-184), the energies of transitions in the time-dependent DFT computed data are recalculated. Within ADF, this kind of calculation is performed as a single-point (ground-state) calculation, by forcing the occupations to contain half an electron less in the donor orbital (according to the transition being explored), and the other half of the electron in the formerly-empty acceptor orbital. This procedure allows exploration of the effects that occur upon the population of the acceptor orbital at the time one of the core electrons is being removed. To study the effect in other transition lines of the same time-dependent DFT calculation, additional jobs need to be performed, which may increase the computation times significantly if all time-dependent DFT lines were to be calculated. Therefore, only the most relevant transition lines are usually recalculated.

In any case, the $\Delta$SCF differences in energy between the acceptor and donor orbitals from the output file of these calculations are used to shift the energy of the corresponding lines of the time-dependent DFT calculated data set, taking one of these $\Delta$SCF differences as a reference. A disadvantage of the method is that it tends to overestimate electronic relaxation. However, even when that is the case, it is already a great method for identifying which transitions are more prone to relaxation effects.

Multiplet simulations are another viable alternative used in the analysis of XAS to explore possible relaxation effects, as discussed in the next section.

4.3. MULTIPLET SIMULATIONS AND XAS

Multiplet simulations have been largely used in the analysis of XAS to investigate multiplet and relaxation effects. As opposed to DFT calculations, multiplet simulations do not represent predictions. Instead, a set of atomic, ligand field and configuration interaction parameters are used to generate, based on first principles, all of the
electronic states involved in a radiative process. These parameters can be modulated and optimised so that the transition lines generated match the experimental data. Once a satisfactory answer is achieved, the parameters used can provide additional meaningful information regarding the interactions in the electronic structure of the ground and excited states (before and after the radiative process occurs).

Another important difference from DFT is that multiplet simulations address the problem from the perspective of electronic states rather than orbitals. This implies that relaxation effects are inherently included.

Using a basis set, either in the LS or jj representation (represented as $\beta$ in Figure 4.6), the electronic multiplets and their corresponding energies are evaluated starting from the electronic configurations $d^N$ and $cd^{N+1}$ in the ground and excited states of a XAS radiative process, respectively (where $c$ denotes a core hole). The matrix elements are evaluated using the irreducible tensor algebra of Wigner and Racah (185-187). The atomic Hamiltonian includes, besides the average energy term for the configurations involved, inter-electronic repulsion and spin-orbit coupling terms that are evaluated using the parameters listed in Table 4.1. Off-diagonal elements are zero for the first term of the Hamiltonian ($H_{\text{ave}}$) but may be significantly different from zero for the other two terms ($H_{ee}$ and $H_{SOC}$), depending on the coupling representation basis set used as well as the relative strength of these two terms. The diagonalisation of the $H_{GS}$ or the $H_{ES}$ matrices gives rise to the atomic multiplets expressed as the linear combinations of the original LS (or jj) basis sets in both the ground and excited state configurations.

In a metal complex, the atomic parameters described on Table 4.1, are used with a reduction factor, $\kappa$, that accounts for nephelauxetic effects. In addition to the atomic terms, a ligand-field potential can be incorporated as part of the Hamiltonian. The basis set under these circumstances needs to be expressed in terms of a given ligand-field representation. Hence, the diagonalisation of the corresponding matrix gives rise to ligand-field multiplets.
Figure 4.6  Generation of atomic multiplets in the ground and excited configurations involved in an XAS radiative process.

\[ \sum_{k=1}^{m} c_{es_{ki}} \left| \gamma J'_{k} \right> = E_{A,es} |\gamma J'_{1}\rangle \]

\[ \sum_{k=1}^{n} c_{gs_{ki}} \left| \gamma J_{k} \right> = d^{N} |\gamma J_{1}\rangle \]

\[ C_{ES}^{T} \cdot H_{ES} \cdot C_{ES} = \Lambda_{ES} \]

\[ C_{GS}^{T} \cdot H_{GS} \cdot C_{GS} = \Lambda_{GS} \]

With,

\[ (H_{GS})_{ij} = \langle \beta J_{i} \ d^{N} | H_{Ave} + H_{ee} + H_{SOC} | \beta J_{j} \ d^{N} \rangle = E_{A,gs} \delta_{ij} + f(\{F_{k}^{}\}) + f(\zeta_{d}) \]

\[ (H_{ES})_{ij} = \langle \beta J'_{i} \ cd^{N+1} | H_{Ave} + H_{ee} + H_{SOC} | \beta J'_{j} \ cd^{N+1} \rangle = E_{A,es} \delta_{ij} + f(\{F_{k}^{},G_{k}^{}\}) + f(\zeta_{d},\zeta_{c}) \]

The computation of the oscillator strength, \( f_{ji,j'j'} \), for each transition line is accomplished by the evaluation of a common matrix \( D \). Considering only the electric-dipole component of light, the matrix elements of \( D \) are evaluated, as shown in Equation 4.4, in an analogous manner to \( f_{jj'} \) in Equation 2.3.

In Equation 4.4, the same ground-state multiplet \( \gamma J_{1} \) is used to transform matrix \( D \) from the left, whereas a different excited-state multiplet \( \gamma J'_{1} \) transforms \( D \) from the right in the computation of each transition-line. The energy for each of these lines is
obtained simply as the subtraction of energies of the multiplets \( \gamma J_i' \) compared with the energy of the ground-state multiplet \( \gamma J_1 \) in the ground-state configuration.

Table 4.1  Atomic, ligand field and VBCI parameters used to generate multiplets in the ground and excited state configurations in the simulation of an XAS radiative process.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>k</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atomic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{A,gs} )</td>
<td>--</td>
<td>Average energy of the ground state configuration (typically set as 0)</td>
</tr>
<tr>
<td>( E_{A,es} )</td>
<td>--</td>
<td>Average energy of the excited state configuration</td>
</tr>
<tr>
<td>( F^K(d) )</td>
<td>2,4</td>
<td>Direct Slater-Condon radial integral</td>
</tr>
<tr>
<td>( F^K(pd) )</td>
<td>2</td>
<td>&quot; (L-edge)</td>
</tr>
<tr>
<td>( G^K(pd) )</td>
<td>1,3</td>
<td>Exchange Slater-Condon radial integral (L-edge)</td>
</tr>
<tr>
<td>( \zeta_d )</td>
<td>--</td>
<td>Spin-orbit coupling in the d-shell</td>
</tr>
<tr>
<td>( \zeta_p )</td>
<td>--</td>
<td>Spin-orbit coupling in the p-shell</td>
</tr>
<tr>
<td><strong>Ligand Field</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \kappa )</td>
<td>--</td>
<td>Nephelauxetic reduction parameter for atomic Slater-Condon integrals and spin-orbit coupling constants</td>
</tr>
<tr>
<td>10Dq, Ds, Dt</td>
<td>--</td>
<td>Crystal field parameters (Oh, Td and D4h symmetries)</td>
</tr>
<tr>
<td>( X_{400}, X_{420}, X_{220} )</td>
<td>--</td>
<td>Crystal Field parameters in Butler’s notation</td>
</tr>
<tr>
<td><strong>VBCI model</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta )</td>
<td>--</td>
<td>Average energy in charge transfer configuration ( (d^{n+1}L ) and ( d^{n-1}L' ) or ( cd^{n+2}L ) and ( cd^{n}L' )) relative to the average energy of base configuration ( (d^n ) or ( cd^{n+1} ))</td>
</tr>
<tr>
<td>( T )</td>
<td>--</td>
<td>Interaction between multiplets in the charge transfer configuration and multiplets in the base configuration.</td>
</tr>
</tbody>
</table>

As described in the following section, bonding, which may offer additional pathways for electronic relaxation, is treated using the VBCI model (see also Section 2.4.3).
Equation 4.4 Oscillator strength calculation for transition lines in a multiplet simulation of XAS.

\[
f_{J_1J'_i}^{1/2} = (\gamma J_1)^T \cdot D \cdot (\gamma J'_i)
\]

\[
= \left( c_{gs11} c_{gs21} c_{gsn1} \right) \cdot \left( \begin{array}{cccc} D_{11} & D_{12} & D_{13} & D_{1m} \\ D_{21} & D_{22} & D_{23} & D_{2m} \\ D_{n1} & D_{n2} & D_{n3} & D_{nm} \end{array} \right) \cdot \left( \begin{array}{c} c_{es1i} \\ c_{es2i} \\ c_{es3i} \\ c_{esmi} \end{array} \right)
\]

With,

\[
(D)_{ij} = D_{ij} = \sqrt{\frac{8 \pi^2 m \nu}{3h}} \sum_q \langle \beta_J_i, d^N | P_q^{(1)} | \beta_J'_j, cd^{N+1} \rangle
\]

4.3.1. The general VBCI model

In the VBCI model, the multiplets of additional charge transfer (typically MLCT or LMCT) configurations are allowed to mix with a base configuration (Figure 4.7). This mixing occurs via off-diagonal matrix elements between multiplets of the charge transfer and the base configurations with the same symmetry, and accounts for electron delocalisation between the valence orbitals of the metal and the valence orbitals in the ligands.

The off-diagonal matrix element resulting from this model emphasizes the coupling between the base and charge transfer configurations and is computed by the mixing parameter, T. Importantly, within this methodology, the electron transferred from the ligand (in the LMCT configuration) to the metal (in the base configuration) is required to have the same symmetry (there is no radiative process involved). Therefore, the off-diagonal matrix elements are given by Equation 4.5, whereas the diagonal matrix elements are given by the average energy of these two configurations, one related to the other, by the parameter \( \Delta \) (Figure 4.7).
Figure 4.7  VBCI model for the mixing of an LMCT charge-transfer configuration with base configuration in the ground and excited states of an XAS radiative process.

\[ C_{Gs}^T \cdot H_{VBCI}^{GS} \cdot C_{Gs} = \Lambda_{GS} \]

\[ C_{Es}^T \cdot H_{VBCI}^{ES} \cdot C_{Es} = \Lambda_{ES} \]

With,

\[ H_{VBCI}^{GS} = \left[ \frac{E_{A,gs}}{\sqrt{10-N}T_{gs}} \right] \]

\[ H_{VBCI}^{ES} = \left[ \frac{E_{A,es}}{\sqrt{10-(N+1)}T_{es}} \right] \]

Ultimately, the diagonalisation of the VBCI interaction matrix in the ground and excited states leads to the VBCI multiplets, expressed as the linear combination of the basis set multiplets in the base and charge transfer configurations. The expansion coefficients in each of these linear combinations provide a measure of covalency.
Equation 4.5  
Off-diagonal matrix elements for the coupling of the charge-transfer configuration with the base configuration in (a) the ground and (b) excited states of an XAS radiative process

\[
\langle d^N | H_{VB CI}^{GS} | d^{N+1} L \rangle = \langle d^{N+1} L | H_{VB CI}^{GS} | d^N \rangle = \sqrt{10 - N} \cdot T_{GS} \quad (a)
\]

\[
\langle c d^{N+1} L | H_{VB CI}^{ES} | c d^{N+2} L \rangle = \langle c d^{N+2} L | H_{VB CI}^{ES} | c d^{N+1} \rangle = \sqrt{10 - (N + 1)} \cdot T_{ES} \quad (b)
\]

In Figure 4.8, a rationalisation for Equation 4.5 is given for the coupling of configurations \(d^7L\) and \(d^6\), as an example.

Figure 4.8  
Coupling of configurations \(d^6\) and \(d^7L\) as a function of hopping parameter \(T\).

As in Equation 4.4, the oscillator strengths for every transition line are computed via the evaluation of a common matrix \(D\), as expressed in Equation 4.6. However, since off-diagonal matrix elements in \(D\) between transitions involving two electrons are equal
to zero, D can be broken down into two smaller matrices \( D_b \) and \( D_{ct} \), for example; \( D_b \)

involving the interaction between the base configuration multiplets, and \( D_{ct} \) involving the interaction between the charge-transfer configuration multiplets of the ground and excited states.

**Equation 4.6**  
Oscillator strength calculation for transition lines involving VBCI multiplets in XAS.

\[
\begin{align*}
J_{i}^{1/2} = & \sum_{j=1}^{n_b+n_{ct}} \sum_{k=1}^{m_b+m_{ct}} (J'_i \cdot J_A^T)_{jk} (D)_{jk} \\
= & \left( (d^N)_{A}^T \cdot D_b \cdot (cd^{N+1})_i + (d^N+1)_{A}^T \cdot D_{ct} \cdot (cd^{N+2}L)_i \right)
\end{align*}
\]

*With,

\[
D = \begin{bmatrix}
D_b & & \\
& & \\
& & D_{ct}
\end{bmatrix}
\]

4.3.2. **Differential orbital covalency**

The computer program originally written by Cowan and later updated by Thole is widely used to run simulations in XAS (Section 2.4.4). The evaluation of covalency for each of the empty orbitals to which the XAS transitions occur is, however, hard to obtain from these simulations by using this program. Erik Wisinger and Frank de Groot reported in a recent paper (139) an approximate method implemented within this computer program to project the intensity of transitions to multiplets into transitions to the different empty orbitals in the system.
The implementation of this method into the Cowan program is in response to the fact that the output on the simulated spectra does not explicitly classify the transitions to multiplets depending on the orbital to which those transitions have occurred. However, if this classification is accomplished beforehand, the evaluation of differential orbital covalency can be more easily extracted.

**Figure 4.9**  VBCI + ligand field multiplet generation in the excited state of a XAS process in a d⁰ octahedral metal complex. The identity and classification of the basis set multiplets 1-6 are given in Figure 4.10.

For instance, in Figure 4.9, the configuration cd¹ in the excited state of a XAS radiative process in a d⁰ octahedral metal complex undergoes mixing with the charge-transfer configuration, cd²L. In this example, an octahedral ligand field along with the VBCI model is considered with electron correlation and spin-orbit coupling parameters turned-off. In addition, the average energy (Eₐ,es) for the base configuration cd¹ has been set to zero.
In this example, the transition lines to the different multiplets are mapped into transitions to orbitals, by separating the multiplets that are known in advance to be populating $t_{2g}$ or $e_g$ orbitals (Figure 4.10) into two separate matrices (Equation 4.7).

**Figure 4.10** Identity of multiplets 1-6 in Figure 4.9 and their classification according to XAS transitions occurring to (a) $t_{2g}$ or (b) $e_g$ orbitals.

Based on this example, the specific models used to generate multiplet simulations for the analysis of the Cl K- and Ru L$_{2,3}$ edges XAS data are discussed in Section 6.1.4.
Equation 4.7

VBCI + LF Hamiltonian corresponding to the computation of multiplets 1-6 in the example considered in Figure 4.9 and its separation into smaller matrices $H_{t^2g}^{ES}$ and $H_{eg}^{ES}$, according to the classification given in Figure 4.10.

$$H_{ES} =
\begin{bmatrix}
-4Dq & 0 & \sqrt{5}T_{t^2g} & 0 & \sqrt{4}T_{eg} & 0 \\
0 & +6Dq & 0 & \sqrt{6}T_{t^2g} & 0 & \sqrt{3}T_{eg} \\
\sqrt{5}T_{t^2g} & 0 & \Delta_{es} - 8Dq & 0 & 0 & 0 \\
0 & \sqrt{6}T_{t^2g} & 0 & \Delta_{es} + 2Dq & 0 & 0 \\
\sqrt{4}T_{eg} & 0 & 0 & 0 & \Delta_{es} + 2Dq & 0 \\
0 & \sqrt{3}T_{eg} & 0 & 0 & 0 & \Delta_{es} + 12Dq
\end{bmatrix}$$

4.4. SIMULATION OF LINE STRENGTHS USING BLUEPRINT XAS

Data consisting of "sticks" (or line strengths), such as the one obtained from time-dependent DFT calculations or TT-Multiplet simulations can be fit to a particular experimental data set using Blueprint XAS. In the current version, plain Matlab code, without a proper GUI is available.

By using this auxiliary code, the user can directly read the energy and oscillator strengths from an output file of the Amsterdam Density Functional (ADF) computational package, the "xy" file from a Cowan-Thole Multiplet calculation, or else the first two columns of a worksheet in Microsoft Excel®. Each transition line is then modelled as a Gaussian, Lorentzian or pseudo-Voigt, but contrary to the regular functions used to fit peaks to the data, the same single parameter is imposed to control the shift of energy
position of all the simulated lines. In a similar way, a scaling factor parameter is used to proportionally amplify the intensity given by the computed oscillator strengths. To account for the shape and width of each line, however, either a single parameter or a modulating function is used.

The use of a modulating function \( f_M \) allows the user to impose a gradual increase/decrease on the shape and width of the lines, depending on the proximity of the function to the inflection point of an edge jump. Four parameters are used to define the widths and/or shapes of all the lines according to this modulating function:

- \( W_{\text{Min}}/G_{\text{Min}} \) (the minimum width or shape);
- \( W_{\text{Max}}/G_{\text{Max}} \) (the maximum width or shape);
- \( LLW/LLG \), the energy, relative to the inflection point of an edge jump (O), at which the width/shape starts to increase/decrease from its minimum/maximum value; and
- \( ULW/ULG \), the energy, relative to the inflection point of the edge jump (O), at which the maximum/minimum width/shaper should be reached (see Figure 4.11).

**Figure 4.11** Modulation function \( f_M \) as used by the auxiliary code for Blueprint XAS to define the width of each transition line.

\[
f_M = \begin{cases} 
W_{\text{Min}}, & x < O - LLW \\
W_{\text{Min}} + (x + LLW - O) \times \frac{W_{\text{Max}} - W_{\text{Min}}}{LLW + ULW}, & O + ULW > x > O - LLW \\
W_{\text{Max}}, & x > O + ULW 
\end{cases}
\]

In theory, a maximum of six peaks are allowed per evaluation function in Blueprint XAS. In practice, a very large number of them is permitted, provided the number of parameters uniquely defined in the "peaks" panel does not exceed 36. Therefore, this auxiliary code distributes the transition-line peaks into six (or fewer) peak functions.
according to the guidelines provided by the user. Each of the peak functions generated this way can be impressively long. However, the number of total parameters, uniquely defined in the "peaks" panel, rarely surpasses 20.

As an example, time-dependent DFT calculations were performed from the crystal structure of the CuCl$_4^{2-}$ moiety of (NEt$_4$)$_2$CuCl$_4$ (Figure 4.4a), using the Amsterdam Density Functional (ADF) 2007.01 software package and the level of theory provided in Sections 4.1.1-4.1.3. In these calculations, the lowest twenty transitions lines originated from the Cl$_{1s}$ orbital of each chlorine atom were computed, for a total of 80 transitions. The results were used to fit the experimental Cl K-edge XAS data set 7 (Figure 3.13) of (NEt$_4$)$_2$CuCl$_4$.

The obtained transition lines were modelled using pseudo-Voigt functions. A single parameter, $O_2$, was used as an energy shift for these lines. Additionally, $I_2$ was set as a scaling factor of all oscillator strengths ($s_i$) and $G_2$ as a constant shape for all of the lines. A modulating function with parameters $W_2$ (WMin), $W_3$ (WMax), $B_1$(LLW) and $B_2$(ULW) was used to define the width of each of the lines about the inflection point of the edge jump, $O_1$. The transition lines were nicely distributed in four peak functions (one for each of the transition-lines sets originated from each of the chlorine atoms).

The evaluation function used in the fitting of the resulting model to the data included not only these four peak functions but also an edge jump, modelled as a cumulative pseudo-Voigt with parameters $I_1$ (Intensity), $O_1$ (Energy inflection point), $G_1$ (Shape), and $W_1$ (hwhm of edge jump), and a switch-like background with two parent functions with parameters $m_1$ (slope), $Y_1$ (Y-intercept) for the first function, and $p_1$ (quadratic coefficient) and $q_1$ (linear coefficient) for the second function (Figure 4.12).

Since this particular problem is highly constrained by the computed transition lines, a single fit is obtained. Table 4.2 lists the "fitoptions" parameters passed on to Matlab to generate this particular fit and Figure 4.13 shows the obtained fit along with the residual data set.
Figure 4.12 Evaluation function for the fitting of time-dependent DFT-computed transition lines to the CI K-edge XAS data set 7 of (NEt₄)₂CuCl₄. The function represented by ‘u’ corresponds to the Heaviside unit step function defined in Equation 2.9.

\[
f = f_e + f_{p_1} + f_{p_2} + f_{p_3} + f_{p_4} + f_b
\]

\[
f_e = I_1(G_1 \cdot C_G + (1 - G_1) \cdot C_L)
\]

\[
C_G = \frac{1}{2}(1 + \text{erf}\left(\frac{x - O_1}{W_1/\ln 2}\right))
\]

\[
C_L = \frac{1}{2}\arctan\left(\frac{x - O_1}{W_1}\right) + \frac{1}{\pi}
\]

\[
f_{p_1-p_4} = I_2 \cdot I_1 \cdot \sum_{i=1}^{20} s_i \cdot (G_2 \cdot F_{G_{p_1-p_4}} + (1 - G_2) \cdot L_{p_1-p_4})
\]

\[
F_{G_{p_1-p_4}} = \sqrt{\frac{\ln 2}{W_{fM}^2 \pi}} \cdot e^{-\frac{(x - E_i - O_2)^2}{W_{fM}^2}}
\]

\[
L_{p_1-p_4} = \frac{1}{\pi} \times \frac{W_{fM}}{(x - E_i - O_2)^2 + W_{fM}^2}
\]

\[
W_{fM} = W_2 \cdot u(O_1 - B_1 - x)
\]

\[
+ \left(W_2 + (E_i + O_2 + B_1 - O_1) \times \frac{W_3 - W_2}{B_1 + B_2}\right) \cdot u(x - O_1 + B_1) \cdot u(O_1 + B_2 - x)
\]

\[
+ W_3 \cdot u(x - O_1 + B_2)
\]

\[
f_b = f_1 \cdot \frac{1}{1 + e^{\frac{(x-O_1)n_3}{W_1}}} + f_2 \cdot \frac{1}{1 + e^{\frac{(O_1-x)n_3}{W_1}}}
\]

\[
f_1 = m_1 \cdot x + YI
\]

\[
f_2 = p_1 \cdot (x - O_1)^2 + q_1 \cdot (x - O_1) + f_1(O_1)
\]

From Figure 4.13 it is evident that the simulated time dependent DFT spectrum does not seem to be fitting the experimental data too well (see also Table 4.3).
Table 4.2  "fitoptions" parameters used in the fitting of computed transition lines to the Cl K-edge XAS data set 7 of \((\text{NEt}_4)_2\text{CuCl}_4\).

<table>
<thead>
<tr>
<th>Parameter name</th>
<th>Value</th>
<th>Parameter name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algorithm</td>
<td>Trust-Region</td>
<td>Robust</td>
<td>On</td>
</tr>
<tr>
<td>DiffMinChange</td>
<td>(10^{-8})</td>
<td>DiffMaxChange</td>
<td>0.1</td>
</tr>
<tr>
<td>MaxIter</td>
<td>2,500</td>
<td>MaxFunEvals</td>
<td>750</td>
</tr>
<tr>
<td>TolFun</td>
<td>(10^{-6})</td>
<td>TolX</td>
<td>(10^{-6})</td>
</tr>
</tbody>
</table>

Figure 4.13  Optimised simulation fit for the Cl K-edge XAS data set 7 of \((\text{NEt}_4)_2\text{CuCl}_4\) from the output of time-dependent DFT calculations displayed in (a) the near-edge region (b) the pre-edge region.
Table 4.3  Results for the fitting of the Cl K-edge XAS data set 7 of (NEt₄)₂CuCl₄, based on 80 time-dependent DFT transition lines computed as detailed in the text.

<table>
<thead>
<tr>
<th>Coefficient parameter</th>
<th>Bounds</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower</td>
<td>Upper</td>
</tr>
<tr>
<td><strong>Edge</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity, I₁</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Inflection point, O₁</td>
<td>2824</td>
<td>2830</td>
</tr>
<tr>
<td>Shape, G₁</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>hwhm Width, W₁</td>
<td>0.1</td>
<td>3</td>
</tr>
<tr>
<td><strong>Background</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m₁</td>
<td>5.00x10⁻⁵</td>
<td>0.002</td>
</tr>
<tr>
<td>Y₁</td>
<td>-5</td>
<td>0</td>
</tr>
<tr>
<td>p₁</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>q₁</td>
<td>-1000</td>
<td>0</td>
</tr>
<tr>
<td><strong>Transition lines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scaling factor, I₂</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>Energy shift, O₂</td>
<td>84</td>
<td>88</td>
</tr>
<tr>
<td>Shape, G₂</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Wmin, W₂</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>Wmax, W₃</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>LLW, B₁</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>ULW, B₂</td>
<td>8</td>
<td>15</td>
</tr>
</tbody>
</table>

The relative energy position of the transition lines for the near-edge feature is overestimated by the DFT calculation, when comparing these to the energy position of the pre-edge transition lines. Furthermore, assuming that self-absorption effects are not significant in the experimental Cl K-edge XAS data set used, either the intensity of the lines comprising the near-edge feature is overestimated, or the intensity of the ones accounting for the pre-edge are underestimated by the DFT calculation under the selected settings.

But the applicability of this tool goes beyond fitting computed transition lines for one compound. In fact, even for this case, each peak function was built using the
transition lines of one of the chlorine atoms in CuCl$_4^{2-}$. This implies that for cases in which the experimental data involves a mixture of species, each peak function can be built using a complete set of lines corresponding to each of these species.

To make this tool of Blueprint XAS more user-friendly, in soon-to-be-released Version 0.3, a GUI replacing the auxiliary code described here will be available.
CHAPTER 5: INSIGHTS INTO CHARGE DONATION PROPERTIES OF PHOSPHINE AND N-HETEROCYCLIC CARBENE LIGANDS

5.1. INTRODUCTION

Trialkylphosphine (PR$_3$) ligands as well as NHC ligands have been the subject of numerous studies over the years, based primarily on the understanding that these ligands are efficient charge donors to metals through $\sigma$-bonding - an aspect that has motivated synthetic chemists to control the reactivity of new or improved transition-metal-based catalysts.

The pioneer work of Tolman with phosphines permitted the development of a methodology that allowed the comparison of the $\sigma$-donation properties of different phosphine ligands. His initial work (188) involved measuring of the $A_1$ vibrational stretching frequency of the carbonyl group ($\nu_{CO}$) in nickel complexes with the general formula Ni(CO)$_2$L, where L is a phosphine ligand. The rationale behind these experiments relies on the idea that as the sigma donation ability from the phosphine ligands increases, the nickel metal is able to back-donate more electron density to the carbonyl groups, in turn weakening the C=O bond and shifting its corresponding vibrational frequency to a lower value.

The observed trends from a large number of phosphine ligands, involving electron-withdrawing, electron-rich, as well as bulky substituents attached to the phosphorous, allowed Tolman to define parameters to approximate the electronic and steric effects in these phosphine systems. The Tolman electronic parameter (TEP) was established based on the experimental $\nu_{CO}$ values for 70 different ligands with different substituents attached to the phosphorous atom (188). To account for steric effects, on the other hand, Tolman defined another parameter known as the cone angle (189). This parameter, which centres the main axis of the cone at the metal-phosphorous bond and encloses the van der Waals surface of the substituents attached to the phosphorous over all orientations, resulted in a useful indicator of reactivity for bulky phosphine
ligands. For example, in general, the cone angle correlates well with phosphine dissociation rates so that the larger the cone angle the faster the dissociation rate observed for this type of ligand in several reactions (189). This observation, however, has not been able to correctly predict the observed trend in, for example, second-generation Grubbs analogues, for which, PCy$_3$ (with a cone angle of 170°) dissociates several times slower than the complex with PPh$_3$ (with a cone angle of 145°) (87). Hence, electronic factors must be also playing a major role in defining the $\sigma$-donation properties of these systems.

More recently, the groups of Herrmann (190) and Nolan (191), influenced by Tolman’s work on phosphines, have used a similar methodology to correlate CO stretching frequencies in nickel and iridium complexes with $\sigma$-donation properties of a large number of NHC ligands. Unfortunately, several assumptions were made that could have influenced the conclusions from these studies. Ultimately, the determination of CO stretching frequencies corresponds to an indirect measure of the net donation from a ligand to the metal. Moreover, the correlation with the CO stretching is not performed by first considering a normal mode analysis to account for the possible coupling of relevant modes of vibration with approximately equivalent or equivalent symmetry. In this regard, the correlation of net donation with a decoupled force constant, and for which possible anharmonic effects are also considered, would be more adequate.

Another important issue with this methodology is that it is assumed a priori that the $\pi$-back bonding properties of phosphine or NHC ligands are negligible, even though this form of bonding can also be affecting the electronic density of the metal in the opposite way that sigma donation does. This assumption is somewhat reasonable when comparing phosphine ligands with bulky and non-withdrawing substituents for which the $\pi$-back bonding is of about the same magnitude. Nevertheless, comparing and combining these results with the obtained for a large and diverse number of NHC ligands might not be as direct and simple as originally anticipated.

After the isolation of the first stable N-heterocyclic carbene by Arduengo III (192) and the subsequent rapid expansion and development of other N-heterocyclic
carbenes (NHCs), they were recognized as strong $\sigma$-donors and considered poor $\pi$-acceptors when bonding to transition metals due to the competing $\pi$-overlap emerging from the electron-rich N atoms (193-198). This assertion has made NHCs highly popular as ancillary ligands in homogeneous catalysts in recent years, displacing phosphines as the preferred ligands in this field. As mentioned earlier in Section 1.3, this idea motivated, for example, the development of the second generation Grubbs catalysts. It was thought at the time that the NHC ligand, by forming a strong Ru-NHC $\sigma$-bond would accelerate the initial phosphine dissociation step (Scheme 1.3). Although the newly synthesized catalysts proved to be more active, it surprisingly showed a slower dissociation step by almost two orders of magnitude. This constituted one of the first observations that challenged the generally accepted nature of the M-NHC bond and opened the door to the importance of other interactions such as $\pi$-back bonding, making these systems more intriguing and interesting than previously anticipated.

In addition to the inclusion of $\pi$-back bonding effects in the model used to compare CO stretching frequencies, the effect of electrostatic interactions has never been explored either. Theoretical studies conducted mainly by Frenking have shown that M-NHC and M-PR$_3$ bonds are both dominated by electrostatic rather than covalent interactions (199-201). Hence, the effect of these electrostatic interactions should be also considered in future CO stretching frequency analyses to improve the accuracy of the obtained results. Another aspect to consider in these studies is the possibility of important differences on the metal charge from compound to compound, particularly when comparing results obtained not only from different kinds of ligands (phosphine versus NHC ligands or unsaturated NHC versus saturated NHC ligands), but also different kinds of metals.

Other studies that compare properties of NHCs and phosphines include the evaluation of reduction potentials (202, 203) in different systems, acidity constants (204, 205) and bond dissociation energies (206). A common conclusion drawn from these studies is that NHC ligands must be better $\sigma$–donors than phosphine ligands. Again, these studies neglect $\pi$-back bonding as well as the possibility of electrostatic interactions when explaining these observed differences. As Frenking and coworkers
have correctly pointed out (201), the results from any of these observables are a consequence of the overall bonding interactions. Furthermore, it has been shown recently (207) through the separation of \( \sigma \)-donation (from ligand to metal) and the \( \pi \)-back donation (from metal to ligand) contributions that the \( \pi \)-acceptance is poorly correlated with the capability of a ligand for \( \sigma \)-donation. Instead, the \( \sigma \)-donation/\( \pi \)-acceptance properties are strongly dependent on the nature of the metal and the other ligands surrounding the metal in a given complex. Therefore, all of the factors affecting the strength of a bond need to be accounted for, in order to draw better conclusions from the CO stretching frequency studies.

In this regard, the research conducted by Bielawski and coworkers is of particular importance and constitutes one of the first studies that prove \( \pi \)-back donation directly as an important bonding component involved in NHC ligation (208). They designed a quinone-annulated NHC that was coordinated to a rhodium complex moiety, \( \text{RhL}_2\text{Cl} \), where \( L \) represents either two carbonyl groups (good \( \pi \)-acceptors) or a cyclooctadienyl ligand (a poor \( \pi \)-acceptor). In the resulting complexes, the stretching frequency of the CO bonds in the quinone, as well as the reduction potential of the quinone-based ligand were measured to explore the changes in the electron density of the \( \pi \)-bonding system in the quinone based ligand. Both experiments showed a richer \( \pi \)-system in the quinone-based NHC when the compound was coordinated to the rhodium complex. This is due to an increase in the \( \pi \)-back bonding from rhodium to the NHC.

In the following sections of this chapter, a direct measure of the charge on the ruthenium metal of carbene-based catalysts, using Ru K-edge XAS, is reported in the context of different ligand environments. Additionally, DFT studies were performed to help with the rationalisation of the experimental results.

### 5.2. ANALYSIS OF RUTHENIUM K-EDGE XAS DATA

To explore the nature of the ligand environment around the ruthenium metal center in compounds 1-7 (Chart 1.1), ruthenium K-edge XAS spectroscopy was used. Of particular interest from this edge, is the investigation of the direct effect on the
ruthenium metal when replacing one of the phosphine ligands by an N-heterocyclic carbene ligand (NHC).

The Ru K-edge XAS data was collected on beamline 7-3, with the experimental set up and conditions given in Section 2.6.1, from samples that were prepared from finely ground powders of each compound. Approximately 5 mg of each compound was mixed with approximately 35 mg of Boron Nitride until a diluted homogeneous mixture as obtained.

Calibration, normalisation, background subtraction and fitting of the obtained spectra were performed by Kendra Getty using traditional approaches and software packages, as described elsewhere (3). This analysis was performed before Blueprint XAS was developed. Fortunately, this kind of spectrum is relatively clean and is dominated by the presence of a very intense edge jump, which facilitates the overall processing with minimal bias and errors in the final results.

5.2.1. Intensity of pre-edge and geometrical considerations

Besides an intense rising edge jump due to the ionisation of the 1s-core electron, the XANES region of a ruthenium K-edge XAS spectrum is characterised by a pre-edge that is due to transitions of an electron from the 1s-core orbital into the low-lying molecular orbitals. From the discussion introduced in Section 2.3, it can be inferred that the intensity of this edge is only noticeable if the amount of Ru-5p character is significant in such molecular orbitals. Otherwise, the transition to Ru-4d based empty orbitals is only electric-quadrupole allowed and several orders of magnitude smaller.

Figure 5.1 compares the normalised Ru K-edge XAS spectrum for compounds 1a-4a. The near-edge region, illustrated in Figure 5.1b, shows a relative intensity of the pre-edge in the order 3a > 2a > 1a > 4a. The same trend is also observed in the case of the second-generation analogues 1b-4b (see Figure 5.3). These results suggest that the pre-edge in these spectra is probably not due to transitions to 5p orbitals (otherwise the observed differences in the intensity among these compounds will be less pronounced). Instead, the differences in intensity reflect the relative amounts of Ru-5p contributions into the Ru-4d based empty molecular orbitals.
Compounds 4a and 4b are nearly octahedral complexes and thus very little mixing of the 5p and 4d ruthenium orbitals can be anticipated. As the distortion from centrosymmetrical geometry becomes more pronounced, the mixing becomes more markedly important and the intensity of the pre-edge increases. As expected, the strong Ru≡C triple bond in complexes 3a and 3b causes the major distortion from centrosymmetry in the series 1-4. The results for the area of the Voigt peaks used to fit the pre-edge in all data sets are consistent with this idea, as shown in Figure 5.1 and Figure 5.3 (see also Table 5.1). In these figures, for clarity, only one pseudo-octahedral pyridine complex was compared with the rest of the compounds in the
series 1-7. Figure 5.2, Figure 5.4 and the corresponding results listed in Table 5.1, however, show very little difference in the intensity of the pre-edge among the pyridine complexes 4-7.

Due to the diversity of geometries and coordination numbers in the series of compounds 1-7, the observations described here can be extended to other species, such as the intermediates involved in the catalytic cycle of ruthenium-based carbene catalysts (see Scheme 1.3). Although the EXAFS analysis for the corresponding Ru K-edge XAS of such species can be more conclusive on determining their geometry, the simple evaluation of the intensity in the pre-edge can provide initial clues on how distorted from centrosymmetry these species might be compared with the compounds considered here.

**Figure 5.2** (a) Extended region, and (b) pre-edge region of the ruthenium K-edge XAS spectra for pyridine-based compounds 1b-4b.
Figure 5.3  (a) Extended region and (b) pre-edge region of the ruthenium K-edge XAS spectra for compounds 4a-7a.

Figure 5.4  (a) Extended region and (b) pre-edge region of the ruthenium K-edge XAS spectra for pyridine-based compounds 4b-7b.
5.2.2. Edge position and metal charge

In addition to the information regarding the degree of distortion extracted from the analysis of the pre-edge, the rising edge provides very valuable information about the charge at the metal centre.

The inflection point of the rising edge at this edge represents a direct measure of the ionisation energy of a core electron from the 1s orbital (IE$_{1s}$). The value of IE$_{1s}$ is in turn proportional to the charge on the metal. Hence, Ru K-edge XAS spectroscopy constitutes a direct probe on how positively charged the ruthenium centre is in complexes 1-7.

Figure 5.5 compares the normalised Ru K-edge XAS spectrum in the near-edge region for compounds 1a and 1b. From Figure 5.5a, it is evident that the rising edge for compound 1b is significantly shifted to higher energy in relation to the position of the edge in compound 1a. This tendency is confirmed by the fitting procedure (Figure 5.5b) and by the second derivative of the data (Figure 5.5c), which consistently show the edge jump to be at higher energy values for 1a than for 1b.

From the fit results given on Table 5.1, the difference between the measured ionisation energies (IE$_{1s}$) for complexes 1a and 1b corresponds to 0.8 eV. Considering that a difference of approximately ~2 eV is typical for changes in oxidation state (209), this difference is quite significant, indicating a more positive ruthenium centre for the second generation catalyst, 1b, but with no difference in oxidation state. Thus, the overall charge donation from the ligands to the metal centre in this compound is significantly less than in the case of 1a. Moreover, because the major difference between 1a and 1b is the replacement of a phosphine ligand by an NHC ligand, these results suggest that the NHC ligand is somehow donating less electron density overall in 1b than the phosphine ligand in 1a, which is contrary to the generally accepted behaviour of the two ligands.

This observation is extended to the analysis of the edge jump in the rest of the compounds in the series 1-7. In all cases, the difference between the IE$_{1s}$ of the first and second generation analogues was always positive, although smaller in magnitude for complexes with higher coordination numbers, likely due to the distribution of the
charge between a larger number of ligands (see Table 5.1, Figure 5.5 - Figure 5.11 [pages 159-166]). The numerical results reported in Table 5.1 were obtained from the fit results (3).

**Figure 5.5** (a) Near-edge Ru K-edge spectra, (b) corresponding fits and (c) second derivatives of the data in the near-edge region for compounds 1a and 1b.

A more positive charge on the ruthenium centre for the second generation pre-catalysts is consistent with the mechanistic observation that the initiation step is faster
for the first generation catalysts than for the second (Section 1.3). Phosphine
dissociation is expected to be slower with a more positive ruthenium centre.

Assuming that contributions from the other ligands remain unchanged between
first- and second-generation analogues, the smaller net-donating behaviour of the NHC
ligand may be due to 1) lower $\sigma$-donation, 2) higher $\pi$-back donation from the metal, or
3) a combination of the two. As described in Section 5.1, previous studies have
concentrated mainly on indirect methods to determine the donation abilities from
phosphine and NHC ligands, focusing mostly on the $\sigma$–donation properties of NHCs,
without necessarily acknowledging their $\pi$-acceptor properties. Recent theoretical work
has shown that another important component of bonding in systems that involve M-PR$_3$
and M-NHC bonds is the electrostatic component.

Table 5.1 Summary of experimental results obtained from the fitting analysis of the
Ru K-edge XAS spectra for compounds 1-7.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Coord. Number</th>
<th>Approx. Symmetry</th>
<th>Area</th>
<th>Pre-edge Energy (eV)</th>
<th>$\Delta$Energy (eV)</th>
<th>IE$_{1s}$ (eV)</th>
<th>$\Delta$IE$_{1s}$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>5</td>
<td>C$_{4v}$</td>
<td>1.9</td>
<td>22164.4</td>
<td>0.5</td>
<td>22122.7</td>
<td>0.8</td>
</tr>
<tr>
<td>1b</td>
<td>5</td>
<td>C$_{4v}$</td>
<td>1.8</td>
<td>22116.9</td>
<td></td>
<td>22123.5</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>4</td>
<td>Cs</td>
<td>1.7</td>
<td>2217.1</td>
<td>0.4</td>
<td>22122.7</td>
<td>1.0</td>
</tr>
<tr>
<td>2b</td>
<td>4</td>
<td>Cs</td>
<td>2.3</td>
<td>22117.5</td>
<td></td>
<td>22123.7</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>5</td>
<td>C$_{4v}$</td>
<td>2.7</td>
<td>22118.4</td>
<td>0.4</td>
<td>22123.4</td>
<td>0.8</td>
</tr>
<tr>
<td>3b</td>
<td>5</td>
<td>C$_{4v}$</td>
<td>3</td>
<td>22118.8</td>
<td></td>
<td>22124.2</td>
<td></td>
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<tr>
<td>4a</td>
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<td>Oh</td>
<td>1</td>
<td>22117.7</td>
<td>-0.2</td>
<td>22123.3</td>
<td>0.2</td>
</tr>
<tr>
<td>4b</td>
<td>6</td>
<td>Oh</td>
<td>1</td>
<td>22117.5</td>
<td></td>
<td>22123.5</td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>6</td>
<td>Oh</td>
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<td>22117.6</td>
<td>-0.1</td>
<td>22122.9</td>
<td>0.4</td>
</tr>
<tr>
<td>5b</td>
<td>6</td>
<td>Oh</td>
<td>1.3</td>
<td>22117.5</td>
<td></td>
<td>22123.3</td>
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<tr>
<td>6a</td>
<td>6</td>
<td>Oh</td>
<td>1.1</td>
<td>22117.6</td>
<td>-0.2</td>
<td>22123.1</td>
<td>0.2</td>
</tr>
<tr>
<td>6b</td>
<td>6</td>
<td>Oh</td>
<td>1.1</td>
<td>22117.4</td>
<td></td>
<td>22123.3</td>
<td></td>
</tr>
<tr>
<td>7a</td>
<td>6</td>
<td>Oh</td>
<td>1</td>
<td>22117.5</td>
<td>-0.1</td>
<td>22123.2</td>
<td>0.1</td>
</tr>
<tr>
<td>7b</td>
<td>6</td>
<td>Oh</td>
<td>1.1</td>
<td>22117.4</td>
<td></td>
<td>22123.3</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.6  (a) Near-edge Ru K-edge spectra and (b) corresponding second derivatives of the data in the near-edge region for compounds 2a and 2b.
Figure 5.7  (a) Near-edge Ru K-edge spectra and (b) corresponding second derivatives of the data in the near-edge region for compounds 3a and 3b.
Figure 5.8  (a) Near-edge Ru K-edge spectra and (b) corresponding second derivatives of the data in the near-edge region for compounds 4a and 4b.
Figure 5.9  (a) Near-edge Ru K-edge spectra and (b) corresponding second derivatives of the data in the near-edge region for compounds 5a and 5b.
Figure 5.10 (a) Near-edge Ru K-edge spectra and (b) corresponding second derivatives of the data in the near-edge region for compounds 6a and 6b.
Figure 5.11 (a) Near-edge Ru K-edge spectra and (b) corresponding second derivatives of the data in the near-edge region for compounds 7a and 7b.
Regardless of the factors influencing the differences on M-PR₃ and M-NHC bonding, the results presented in this section are all consistent with a more positive ruthenium centre in the presence of an NHC ligand.

5.2.3. DFT calculations

To explore the possible source of charge donation differences between first- and second-generation analogues, DFT calculations were performed for compounds 1-5.

The first important task in defining the DFT model was to undergo a DFT geometry optimisation in the first- and second-generation analogues of complexes 1-5. Based on previous DFT studies in metal complexes, a VNW/BP86 functional was used in all cases, as described in Section 4.1.1.

Level of theory

In the case of compound 1b and 2b for which a crystal structure was available, the optimised geometry using two different levels of theory - one with TZP and the other with TZ2P basis set - were compared to the corresponding crystal structure. In both cases a final integration level of 6.0 was achieved. In the case in which a TZP basis set was used, an effective core potential (ECP) was used in the ruthenium atom, as described in Section 4.1.3. No effective core potentials in any of the atoms were employed in the case in which a TZ2P was used.

Table 5.2 lists the bond distances for the atoms involved in the first coordination sphere in the crystal structure, as well as the bond distances in the TZP and TZ2P optimised geometries for compound 1b. In addition, Figure 5.12a illustrates the alignment of the optimised structures with the crystal structure (excluding hydrogen atoms only) at their maximum values of similarity index ($I_S$), whereas in Figure 5.12b, only the alignment of the main coordination sphere is shown at their maximum values of $I_S$. Although a closer agreement between the model and the crystal structure is obtained with the use of a TZ2P basis set, the results were not significantly different from those obtained using a TZP basis set. These observations were similarly present in the case of compound 2b (see Table 5.3 and Figure 5.13). Hence, a TZP basis set with an ECP for ruthenium was determined to be a sufficient level of theory for the
ground state calculation discussed in the following section. For consistency, time-dependent DFT calculations were also computed using the same level of theory.

**Table 5.2** Bond distances for the main coordination sphere in DFT-TZP and DFT-TZ2P optimised geometries compared to corresponding internal coordinates in the crystal structure of compound 1b (C₂ = Main carbon atom in alkylidene group)

<table>
<thead>
<tr>
<th>Bond distance</th>
<th>Crystal Structure</th>
<th>TZP Optimised Geometry</th>
<th>TZ2P Optimised Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-Cl₁</td>
<td>2.3911</td>
<td>2.4498</td>
<td>2.4266</td>
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<tr>
<td>Ru-Cl₂</td>
<td>2.3988</td>
<td>2.4655</td>
<td>2.4421</td>
</tr>
<tr>
<td>Ru-P</td>
<td>2.4245</td>
<td>2.4896</td>
<td>2.4580</td>
</tr>
<tr>
<td>Ru-C₁</td>
<td>2.0846</td>
<td>2.1143</td>
<td>2.1216</td>
</tr>
<tr>
<td>Ru-C₂</td>
<td>1.8348</td>
<td>1.8732</td>
<td>1.8611</td>
</tr>
</tbody>
</table>

**Table 5.3** Bond distances for the main coordination sphere in DFT-TZP and DFT-TZ2P optimised geometries compared to corresponding internal coordinates in the crystal structure of compound 2b (C₂ = Main carbon atom in alkylidene group)

<table>
<thead>
<tr>
<th>Bond distance</th>
<th>Crystal Structure</th>
<th>TZP Optimised Geometry</th>
<th>TZ2P Optimised Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-Cl₁</td>
<td>2.2810</td>
<td>2.3404</td>
<td>2.3231</td>
</tr>
<tr>
<td>Ru-Cl₂</td>
<td>2.2950</td>
<td>2.3266</td>
<td>2.3121</td>
</tr>
<tr>
<td>Ru-C₁</td>
<td>1.9877</td>
<td>2.0097</td>
<td>2.0081</td>
</tr>
<tr>
<td>Ru-C₂</td>
<td>1.8167</td>
<td>1.8460</td>
<td>1.8321</td>
</tr>
</tbody>
</table>

**Ground-state DFT results**

Ground state DFT calculations were performed from the TZP-optimised geometry for compounds 1-5. From the analysis of the results obtained in the output of these calculations, the Mulliken and multipole analysis derived charges (MCD) are consistent with the experimental evidence: a more positive ruthenium centre was obtained in the case of the second-generation analogues (see Table 5.8).
Figure 5.12 Comparison between the crystal structure (dark grey) and the TZP (light grey) and TZ2P (grey) optimised geometries for compound 1b: (a) Full optimised geometries and (b) first-coordinating sphere in optimised geometries aligned relative to a static crystal structure (Cr) at maximum values of the corresponding similarity index.

\[ I_{S_{cr,TZP}} = 0.9115 \]

\[ I_{S_{cr,TZ2P}} = 0.9125 \]

\[ I_{S_{cr,TZP}} = 0.9806 \]

\[ I_{S_{cr,TZ2P}} = 0.9861 \]
Figure 5.13 Comparison between the crystal structure (dark grey) and the TZP (light grey) and TZ2P (grey) optimised geometries for compound 2b: (a) Full optimised geometries and (b) first-coordinating sphere in optimised geometries aligned relative to a static crystal structure (Cr) at maximum values of the corresponding similarity index.

From atomic and fragment contributions in the low-lying molecular orbitals, the Ru-5p contribution is of approximately the same magnitude for compounds 1a-3a (16%, 11% and 13%; Table 5.4 [Page 174]) and for compounds 1b-3b (16%, 15% and 16%; Table 5.5 [Page 178]). Consistent with the experimental results, these Ru-5p contributions are higher than the values obtained for the pseudo-octahedral
compounds 4a, 5a (3%; Table 5.6 [Page 182]) and 4b, 5b (6% and 9%; Table 5.7 [Page 185]). Interestingly, in all cases, the greatest 4d-5p mixing occurs within the Ru-4d based orbital involved in $\sigma$-bonding with the alkylidene carbon atom, suggesting the direction of the ruthenium-carbene sigma bond as the primary source of distortion from centrosymmetry. To further clarify this observation, Figure 5.14a shows how, as the interaction of the metal with the ligands becomes more directional and preferential in one direction (along the ruthenium-carbene sigma bond), the amount of Ru-5p increases. Furthermore, Figure 5.14b shows isosurface plots for relevant orbitals in the series 1a-4a. As is evident from this figure, the strong interaction along the Ru-carbene sigma bond is indeed the major source for the distortion observed mostly in compounds 1-3.

An interesting aspect that is evident from the molecular orbital (MO) diagrams of compounds 1-4, is the observed differences in the $\pi$-interaction between the ruthenium atom and the alkylidene carbon. For compounds 1a (MOs 202 a$_1$ and 206 a$_1$; Figure 5.15 [Page 175]), 1b (MOs 206 a$_1$ and 211 a$_1$; Figure 5.18 [Page 176]), and similarly for compounds 4-7, this bonding system is effected by the interaction of a ruthenium-4d orbital with an empty $\pi^*$ anti-bonding orbital in the alkylidene fragment. Nevertheless, in the case of Pier’s analogues, this $\pi$-bonding system (e.g., MOs 147 a$_1$ and 185 a$_1$ of Figure 5.16 [Page 176] for 2a) involves the interaction with a non-bonding orbital localised mostly in the phosphonium-alkylidene carbon. The non-bonding nature of this orbital and the positive charge in the corresponding fragment, allows for a stronger interaction with the ruthenium 4d orbitals. Accordingly, although the carbene in 2a, 2b remains a Fischer-type carbene, the $\pi$-bonding system starts to resemble that of a Schrock-type carbene (Figure 1.1).

In compounds 3a (Figure 5.17 [Page 177]) and 3b (Figure 5.20 [Page 181]), where there are two $\pi$-bonding systems, the carbon-2p orbitals involved in the $\pi$-interactions are close in energy to the Ru-4d orbitals and, since the carbon atom is only mixing with ruthenium, each of these interactions is considerably stronger than in compounds 1 and 2; strong enough to cause an important change in the nature of the lowest unoccupied molecular orbital (LUMO).
Figure 5.14 Relationship between Ru-5p mixing in ruthenium 4d-based orbitals and distortion from centrosymmetry. (a) As the interaction of the ruthenium centre becomes increasingly more significant in one direction (along the Ru-carbene sigma bond), the amount of Ru-5p increases. (b) A significant amount of Ru-5p is observed from DFT calculations in compounds 1a-3a resulting in a strong distortion along the direction of the ruthenium-carbene sigma bond.

On the other hand, when comparing the MO diagrams for the first-generation analogues (Figure 5.15 -Figure 5.17 [Pages 175-177] and Figure 5.21-Figure 5.22 [Pages 183-184]) with those for the corresponding second-generation analogues (Figure 5.18-Figure 5.20 [Pages 179-181] and Figure 5.23-Figure 5.24 [Pages 186-187]), it is worth noting that there are relatively few differences in the overall bonding
manifold. This supports the idea that the overall ligand field remains mostly the same in each case, with differences localized in the bond between the metal and the ancillary ligands. This further implies that the differences in the charge of the ruthenium centre originate primarily from the differences in charge donation from phosphine ligand compared with that from the NHC ligand. As shown in Table 5.4-Table 5.7 (Pages 174,178,182,185), the results from these calculations indicate larger charge donation from the PCy₃ ligand into the Ru-4dₜσ* based orbitals of the first-generation analogues, compared with the charge donation from the NHC ligand in the second-generation counterparts. Moreover, the second-generation analogues exhibit an important charge donation from the ruthenium centre to the π-back bonding orbital of the NHC ligand in all cases, and only a smaller contribution to the π-back bonding of phosphine ligands. The sum of these two effects adds up to the total difference on the charge of the ruthenium centre summarised in the last column of Table 5.8 (Page 188). The results of this analysis in the low-lying empty MOs reflect a more positive ruthenium centre for the second-generation analogues. As noted experimentally, the differences are somewhat smaller in the bispyridine complexes, where the greater coordination number is expected to mitigate the effect of a single ligand. Interestingly, increasing coordination number does little to change π-back bonding contributions but has a significant impact on σ-donation.

A recent publication that employs a similar analysis based on fragment contributions for compounds 1a and 1b, known as energy decomposition analysis (EDA), is consistent with the results presented here (210). Their estimation of the ligand to ruthenium σ-donation consisted of a modified EDA procedure that involved only the inclusion of empty molecular orbitals where Ru 4dₜσ* has an important contribution. Similarly, the estimation of the ruthenium to ligand π-back donation included only those orbitals with important contributions from the out-of-plane pₓ-type orbitals, based on the respective ligand fragments. Their results indicated that while the NHC ligand is significantly more tightly bonded to ruthenium than the PCy₃ ligand, with an important electrostatic component in both cases, the NHC ligand exhibited smaller σ-charge donation and greater π-acceptance than the PCy₃ ligand.
Table 5.4 Energies and atomic or fragment orbital contributions of relevant molecular orbitals from the ground state DFT calculation of compounds (a) 1a, (b) 2a, and (c) 3a. Darker cells indicate higher atomic/fragment contributions.

(a)

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<th>Orbital</th>
<th>Energy(eV)</th>
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<th>Carbene</th>
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<td>18%</td>
<td>3%</td>
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<td>1%</td>
<td>30%</td>
<td>3%</td>
</tr>
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(b)

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(c)

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Figure 5.15 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 1a. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e/Å³.
Figure 5.16 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 2a. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e/Å$^3$.
Figure 5.17 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 3a. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e⁻/Å³.
Table 5.5  Energies and atomic or fragment orbital contributions of relevant molecular orbitals from the ground-state DFT calculation of compounds (a) 1b, (b) 2b, and (c) 3b. Darker cells indicate higher atomic/fragment contributions.

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Figure 5.18 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 1b. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e/Å$^3$. 
Figure 5.19 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 2b. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e/Å³.
Figure 5.20 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 3b. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e⁻/Å³.
Table 5.6  Energies and atomic or fragment orbital contributions of relevant molecular orbitals from the ground-state DFT calculation of compounds (a) 4a and (b) 5a. Darker cells indicate higher atomic/fragment contributions.

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Figure 5.21 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 4a. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e⁻/Å³.
Figure 5.22 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 5a. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e⁻/Å³.
Table 5.7  Energies and atomic or fragment orbital contributions of relevant molecular orbitals from the ground-state DFT calculation of compounds (a) 4b and (b) 5b. Darker cells indicate higher atomic/fragment contributions.

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<td>210a1</td>
<td>−2.15</td>
<td>5%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>211a1</td>
<td>−1.92</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>213a1</td>
<td>−1.48</td>
<td>41%</td>
<td>0%</td>
<td>18%</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>222a1</td>
<td>−0.55</td>
<td>4%</td>
<td>2%</td>
<td>0%</td>
<td>60%</td>
<td>8%</td>
</tr>
<tr>
<td>223a1</td>
<td>−0.10</td>
<td>31%</td>
<td>7%</td>
<td>0%</td>
<td>3%</td>
<td>7%</td>
</tr>
</tbody>
</table>
Figure 5.23 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 4b. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e⁻/Å³.
Figure 5.24 Simplified molecular orbital diagram displaying the DFT-calculated valence electronic structure for compound 5b. Isosurface plots for empty molecular orbitals are displayed using a density of 0.05 e⁻/Å³.
Table 5.8  DFT-calculated charges and summary of charge distribution analysis from empty valence orbitals for compounds 1-5.

<table>
<thead>
<tr>
<th>Complex</th>
<th>MDC Charges</th>
<th>Mulliken Charges</th>
<th>Ru 4d Occupation</th>
<th>Ru 5p Occupation</th>
<th>Ligand to Metal 4σ* charge donation</th>
<th>π back-bonding charge donation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qRu</td>
<td>ΔqRu</td>
<td>qRu</td>
<td>ΔqRu</td>
<td>Occupation</td>
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</tr>
<tr>
<td>1a</td>
<td>1.45</td>
<td>+0.26</td>
<td>0.37</td>
<td>+0.27</td>
<td>7.06</td>
<td>0.47</td>
</tr>
<tr>
<td>1b</td>
<td>1.71</td>
<td>0.64</td>
<td>6.94</td>
<td>0.34</td>
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<td>0.1</td>
</tr>
<tr>
<td>2a</td>
<td>1.78</td>
<td>+0.37</td>
<td>0.54</td>
<td>+0.31</td>
<td>6.94</td>
<td>0.47</td>
</tr>
<tr>
<td>2b</td>
<td>2.15</td>
<td>0.85</td>
<td>6.83</td>
<td>0.41</td>
<td>0.38</td>
<td>0.12</td>
</tr>
<tr>
<td>3a</td>
<td>1.64</td>
<td>+0.29</td>
<td>0.16</td>
<td>+0.29</td>
<td>6.93</td>
<td>0.66</td>
</tr>
<tr>
<td>3b</td>
<td>1.93</td>
<td>0.45</td>
<td>6.84</td>
<td>0.53</td>
<td>0.7</td>
<td>0.16</td>
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<tr>
<td>4a</td>
<td>1.62</td>
<td>+0.18</td>
<td>0.85</td>
<td>+0.26</td>
<td>6.9</td>
<td>0.3</td>
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<td>4b</td>
<td>1.80</td>
<td>1.11</td>
<td>6.81</td>
<td>0.17</td>
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<td>5a</td>
<td>1.62</td>
<td>+0.22</td>
<td>0.82</td>
<td>+0.25</td>
<td>6.91</td>
<td>0.3</td>
</tr>
<tr>
<td>5b</td>
<td>1.84</td>
<td>1.07</td>
<td>6.83</td>
<td>0.18</td>
<td>0.3</td>
<td>0.12</td>
</tr>
</tbody>
</table>

In summary, the analysis of the pre-edge in the Ru K-edge XAS data has shown that this feature is sensitive to the amount of Ru-5p mixing and that this in turn reflects the degree of distortion from centrosymmetry in complexes 1-7. Hence, the intensity of this pre-edge of the Ru K-edge XAS could serve as a good initial measure when studying the geometry of intermediates in olefin metathesis or other related species for which their structural information is unknown.

Furthermore, from the analysis of the Ru K-edge XAS data, the experimental results obtained for the ionisation energy (IE₁s) indicated a more positive ruthenium centre for the second-generation analogues. In addition, the intensity of the pre-edge is of about the same magnitude when comparing first and second generation analogues, particularly in the case of compounds 1, and 4-7. This suggests that the ruthenium-carbene interaction, as the major source of distortion in these complexes, remains of more or less the same magnitude upon the substitution of the ancillary ligand. Ground-state DFT calculations are consistent with these observations by confirming the differences in charge on the metal centre. Moreover, these calculations provide some
insights into the origin of these differences by revealing significant \( \pi \)-back donation from the metal to the NHC ligand and reduced \( \sigma \)-donation to the metal compared with that from the PCy\(_3\) ligand.

Overall, these results suggest that NHC ligands are not necessarily better charge donors than phosphine ligands and provide a compelling rationale for the previously observed kinetic results in the Grubbs catalyst: the initial phosphine-dissociation step is slower for the complex with the more-positively charged metal centre. This rationale can be extended to other systems in organometallic chemistry to explain similar observed trends (211, 212) and to revisit the conclusions drawn from CO stretching data, according to improved bonding models for these systems.
CHAPTER 6: MULTIPLE-EDGE XAS ANALYSIS AND ELECTRONIC STRUCTURE OF RUTHENIUM-BASED CATALYSTS

Although the Ru K-edge XAS analyses from the previous chapter provides crucial insights into the electronics of ruthenium carbene-based catalysts, they provide a one-dimensional view of their overall electronic structure. The exploration of complementary XAS edges permits a more complete experimental investigation of these compounds.

The well-established Cl K-edge XAS analysis permits the evaluation of covalency in the M-Cl bonds and is ideal in the determination of the total amount of chlorine present in the ruthenium-based low-lying MOs. Analysis of Ru L-edge XAS data, on the other hand, allows for a more general ligand field analysis of the metal centre and ligand contributions. With the additional analysis of the C K-edge XAS data, as well as with the aid of computational methods, the electronic structure of the low-lying empty MOs in these catalysts can be ultimately determined from several perspectives around the metal centre.

6.1. ANALYSIS OF THE Cl K- AND Ru L_{2,3}- EDGES XAS SPECTRA

The analysis of the Cl K-edge has proven to be more difficult than originally anticipated. As described earlier (Sections 2.7.3 and 3.1), the overlap of this edge with the Ru L-edge and a challenging background made necessary the development of novel methodologies that ultimately triggered the creation of Blueprint XAS.

6.1.1. Early models

The handle-like background model (Section 2.7.3) was an important element of the methodology used to analyse Cl K- and Ru L-edges XAS data sets on the Grubbs (1a,1b) and Piers (2a,2b) first- and second-generation analogues. The initial step of this methodology (1) consisted in the background subtraction of a handle-like function that was optimised with respect to the final background-subtracted spectra by seeking flat plateaus in the quasi-linear regions, via a least-squares minimisation procedure (Equation 2.8).
The analysis continued with the fitting of the background-subtracted data sets, by using a traditional methodology in PeakFit®. The start point for the evaluation function prior to each fit was user-selected.

A very early attempt in the deconvolution of the two edges involved the assumption that the ratio between the Ru L$_3$- and L$_2$-edges ($\lambda_{\text{Ru-L}_3/L_2}$) follows a statistical 2:1 value, a typical practical measure used in the multiplet-based analysis of early transition metal L-edge XAS data (135, 136, 139) (see also Sections 2.5 and 4.4). The fitting of the corresponding evaluation function, however, never gave reasonable answers. A more suitable ratio for these compounds was accomplished with the analysis of the data for the chlorine-free compound 8. As mentioned in Section 3.6.6, a value of 1.74 was obtained for $\lambda_{\text{Ru-L}_3/L_2}$. Although not explicitly defined in the evaluation function, an additional constraint was used to fit the rest of the data for compounds 1 and 2: a common ratio between the intensities of the Cl K- and Ru L$_{2,3}$-edges ($\lambda_{\text{Cl-K/Ru-L}}$) was searched. The rationale behind this constraint relied on the assumption that since the ratio between the number of chlorine and ruthenium atoms in these complexes is the same, so the ratio between the corresponding edge jumps should also be the same.

In addition to these constraints, the evaluation function included three cumulative pseudo-Voigt functions that modelled the Ru L- and Cl K-edge jumps, respectively, as well as two Voigt functions that modelled the pre-edge and near-edge features in the Cl K-edge of compounds 1a and 1b. An additional Voigt peak was used to model the shoulder of the pre-edge that is visible in compounds 2a and 2b. Other peak functions around the Ru L-edge were used, but only to support the overall model by better defining the intensities of the two edge jumps around the Ru L-edge.

The final step of the procedure involved the normalisation of each spectrum and the peak functions in the Cl K-edge. The intensity of the obtained edge jump for the Cl K-edge was used for this purpose. The results of the analysis are listed in Table 6.1 (Page 194) and the obtained normalised spectra for compounds 1 and 2 are shown, respectively, in Figure 6.1 (Page 192) and Figure 6.2 (Page 193). For comparison, the
ionisation energy for the Cl-1s electrons ($IE_{Cl,1s}$) obtained from the first derivative of the original calibrated spectra is also listed in

Table 6.1 (Page 194).

**Figure 6.1**  Normalised spectra for (a) compounds 1a (black dots) and 1b (grey dots). Fit to the Cl K-edge XAS spectrum of (b) 1a and (c) 1b.
Figure 6.2  Normalised spectra for (a) compounds 2a (black dots) and 2b (grey dots). Fit to the Cl K-edge XAS spectrum of (b) 2a and (c) 2b.
Table 6.1  Fit results for background-subtracted Cl K- and Ru L-edges XAS data sets of compounds 1,2 and 8.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IE_{Cl,1s}</th>
<th>IE_{Cl,1s}, Fit</th>
<th>IE_{Cl,1s}, 1st derivative</th>
<th>\lambda_{Ru,L_3/L_2}</th>
<th>\lambda_{Cl,K/Ru,L}</th>
<th>I_{\psi--Cl1s}^{(Pre-edge)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2825.0</td>
<td>2825.3</td>
<td>(1.74)</td>
<td>0.67</td>
<td>2.68</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>2824.9</td>
<td>2825.6</td>
<td>(1.74)</td>
<td>0.69</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>2825.8</td>
<td>2826.2</td>
<td>(1.74)</td>
<td>0.68</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>2826.0</td>
<td>2826.6</td>
<td>1.73</td>
<td>0.69</td>
<td>2.88</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>1.74</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. In the case of compounds 1a and 1b, the intensity is calculated from the normalised area below the fitted f_{P1} function. In the case of compounds 2a and 2b, this quantity is computed using the normalised area below fitted functions f_{P1} and f_{P2}.

6.1.2. Recently developed model

Additional data taken at a later time for compounds 1-8 show the expected features for compounds 1-2 at about the same energies as in the samples used in the previous analysis (see below). The relative intensities of these features were, however, significantly different in the new data. The values for \lambda_{Ru\,L_3/L_2} and \lambda_{Cl\,K/Ru\,L} were different from the previously obtained results and not consistent between the data of different compounds, suggesting that distortion effects may be causing the observed discrepancies. Therefore, a new model that uses no constraints in any of these ratios was required.

Based on the model developed to fit the data for compound 8 (Section 3.6.6), a new model was developed to fit the data for chlorine-containing compounds 1-7. The evaluation function of this model, shown in Figure 6.3 (Page 195) and expressed in Equation 6.1 (Page 196) for compound 1a, correlates the intensity of the Ru-L_3 and Ru-L_2 edge jumps and the intensities of each equivalent near-edge features in these two edges by using the same parameter, denoted in Equation 6.1 as B_1 (\lambda_{Ru\,L_3/L_2}). This measure alone represents a robust constraint that permits the deconvolution of the Cl K- from the Ru L-edge.

In addition, another parameter, denoted as W_2 in Equation 6.1 (or also as \Delta in Figure 3.26) and related to the Ru-2p spin-orbit coupling, is used to correlate the energies of any two equivalent features in the Ru L_2^- and L_3-edges, reducing the
number of parameters in the overall model and helping define the energy position of each edge jump in the Ru L-edge.

**Figure 6.3** Components of evaluation function used for fitting the Cl K- and Ru L\(_{2,3}\)-edges XAS data sets of compound 1a.
Equation 6.1 Evaluation function for the fitting of the Cl K- and Ru L\textsubscript{2,3}-edges XAS data sets of compound 1a.

\[ f = f_b + f_{e1} + f_{e2} + f_{P1} + f_{P2} + f_{P3} + f_{P4} + f_{P5} \]

Where,

\[ f_b = f_1 \cdot U(O_2 - x, W_3) + f_2 \cdot U(x - O_2, W_3) \cdot U(O_2 + W_2 - x, W_3) + f_3 \cdot U(x - O_2 - W_2, W_3) \]

\[ U(x - b, W_3) = \frac{1}{1 + e^{-\frac{ln(6 - x)}{W_3}}} \]

\[ f_1 = m_1 x + YI; \quad f_2 = m_2 (x - O_1) + f_1 (O_1); \quad f_3 = m_3 (x - O_1 - W_2) + f_2 (O_1 + W_2) \]

\[ f_{e1} = I_1 \left[ G_1 \cdot \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - O_1}{W_1 \cdot \ln 2} \right) \right] + (1 - G_1) \cdot \left( \frac{1}{2} \text{arctan} \left( \frac{x - O_1}{W_1} \right) + \frac{1}{\pi} \right) \right] \]

\[ f_{e2} = B_1 \cdot I_2 \left[ G_2 \cdot \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - O_2}{W_2} \right) \right] + (1 - G_2) \cdot \left( \frac{1}{2} \text{arctan} \left( \frac{x - O_2}{W_2} \right) + \frac{1}{\pi} \right) \right] \]

\[ + I_2 \left[ G_2 \cdot \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - O_2}{W_3 \cdot \ln 2} \right) \right] + (1 - G_2) \cdot \left( \frac{1}{2} \text{arctan} \left( \frac{x - O_2}{W_2} \right) + \frac{1}{\pi} \right) \right] \]

\[ f_{P1,2} = I_{3,4} \cdot I_1 \left[ G_{3,4} \cdot \sqrt{\frac{\ln 2}{W_{2,5}^2}} \cdot e^{-\frac{\ln 2(x - O_{3,4})^2}{W_{2,5}^2}} + \frac{1 - G_{3,4}}{\pi} \times \frac{W_{4,5}}{(x - O_{3,4})^2 + W_{4,5}^2} \right] \]

\[ f_{P3,4,5} = B_1 \cdot I_{5,6,7} \cdot I_2 \left[ G_{5,6,7} \cdot \sqrt{\frac{\ln 2}{W_{2,7,8}^2}} \cdot e^{-\frac{\ln 2(x - O_{5,6,7})^2}{W_{2,7,8}^2}} + \frac{1 - G_{5,6,7}}{\pi} \times \frac{W_{6,7,8}}{(x - O_{5,6,7})^2 + W_{6,7,8}^2} \right] \]

\[ + I_{5,6,7} \cdot I_2 \left[ G_{5,6,7} \cdot \sqrt{\frac{\ln 2}{W_{2,7,8}^2}} \cdot e^{-\frac{\ln 2(x - O_{5,6,7} - W_2)^2}{W_{2,7,8}^2}} + \frac{1 - G_{5,6,7}}{\pi} \times \frac{W_{6,7,8}}{(x - O_{5,6,7} - W_2)^2 + W_{6,7,8}^2} \right] \]

The implementation of the switch-like background as part of the evaluation function further imposes a constraint on the energy positions of all the edge jump functions in the model and allows evaluation of the impact on background subtraction prior to fitting procedures. Finally, the possibility of generating multiple independent fits using Blueprint XAS yields a more robust analysis of each data set. These latter considerations are important especially in cases where the presence of shoulder peaks or other features are not well-resolved multiply the number of good physically-viable solutions and inherently increase the uncertainty on parameters defining each of these.
features. Hence, the implementation of this model in Blueprint XAS is useful to estimate such uncertainties, to evaluate the quality of each individual data set and to test the robustness of the evaluation function itself.

### 6.1.3. Analysis and fitting results

A model based on the evaluation function discussed in the previous section was built to fit several Cl K- and Ru L₂,3-edges XAS data sets for compounds 1 and 2. Table 6.2 (Page 198) lists the number of data sets analysed, the sample preparation conditions, and the date for the collection of each data set. For reference, the first data sets listed in this table correspond to the same data sets employed in the analysis discussed in Section 6.1.1 for compounds 1-2. A total of 100 independent fits were computed for each data set using the same evaluation function for samples of the same compound.

Even though each peak was internally normalised (Section 3.5), for visual purposes each data set was background subtracted and normalised after the fitting procedure using the post-fitting toolbox for Blueprint XAS.

Moreover, the specific analysis of the Cl K-edge XAS was complemented by time-dependent DFT calculations using the level of theory described in Section 5.2.3. In each case, the lowest 40 transitions, which originate from the 1s orbital of the chlorine atoms were computed from the corresponding TZP-optimised geometry. With respect to the calculated energies corresponding to transitions to the lowest Ru-4d based empty MO, the Slater $\Delta$SCF corrections in the energy of each transition to the remaining low-lying empty MOs was also computed to account for electronic relaxation effects.

**First generation Grubbs catalysts, 1a**

Figure 6.4 (Page 199) shows a representative example for the fitting of one data set in compound 1a, showing relevant components of the evaluation function in the Cl K- and Ru L₃- edges. Figure 6.5 (Page 200) displays the normalised data sets 1-6, Table 6.3 (Page 201) lists the fit results for parameters relevant to the Cl K-edge, and
Table 6.4 (Page 201) lists the fit results for relevant parameters in the Ru L-edge for data sets 1-6 of compound 1a.

**Table 6.2** Sample preparation and data collection details for Cl K-edge and Ru L_{2,3}-edges XAS data sets relevant to this thesis work.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Data set</th>
<th>Collection date</th>
<th>Beamline</th>
<th>Preparation details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1</td>
<td>April 2005</td>
<td>6-2</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>January 2007</td>
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<td>3</td>
<td>March 2009</td>
<td>4-3</td>
<td>B, 90:10</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>March 2009</td>
<td>4-3</td>
<td>B, 50:50</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>March 2009</td>
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<tr>
<td></td>
<td>6</td>
<td>March 2009</td>
<td>4-3</td>
<td>B, 15:85</td>
</tr>
<tr>
<td>1b</td>
<td>1</td>
<td>April 2005</td>
<td>6-2</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>2</td>
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<tr>
<td></td>
<td>4</td>
<td>March 2009</td>
<td>4-3</td>
<td>B, 50:50</td>
</tr>
<tr>
<td>2a</td>
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</tr>
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<td>B, 50:50</td>
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</tr>
<tr>
<td></td>
<td>4</td>
<td>March 2009</td>
<td>4-3</td>
<td>B, 50:50</td>
</tr>
</tbody>
</table>

A. About 5 mg of sample are finely ground. The obtained powder is spread over Kapton® tape, creating a homogeneous thin film over it.

B. Before spreading over Kapton tape, a small amount of sample is diluted with boron nitride (BN) in the indicated sample:BN proportion, by volume (v:v).

From the fit results listed on Table 6.3 and Table 6.4 for the first data set, it is worth noticing the remarkably good agreement of the obtained value for the Ru L_{3}/L_{2} intensity ratio (B_{1} =1.73 ± 0.01; Table 6.4) with the one previously obtained from early developed methodologies (λ_{Ru}L_{3}/L_{2} = 1.74; Table 6.1) - an observation that has been addressed also for the fit results in compound 8 (Section 3.6.6). These combined results support the idea that background subtraction procedures prior to fitting do not
impact significantly the final results in the analysis of concentrated samples (see also Section 3.6.5).

**Figure 6.4** Representative fit to a Cl K- and Ru L-edges XAS data set of compound 1a, showing the relevant components in the evaluation function in the region near (a) the Cl K-edge and (b) the Ru L$_3$-edge.
Figure 6.5 Normalised Cl K- and Ru L$_{2,3}$-edges XAS spectra for samples 1 (darker) - 6 (lighter) in compound 1a, showing (a) the region near the Cl K-edge, (b) the region involving all spectral features and (c) the region near the Ru L-edge.
### Table 6.3
Fit results for relevant parameters corresponding to features in the Cl K-edge region of the Cl K- and Ru L_{2,3}-edges XAS data sets 1-6 for compound 1a.

<table>
<thead>
<tr>
<th></th>
<th>$E_{e1}$ (eV)</th>
<th>$I_{P1}$ (normalised)</th>
<th>$E_{P1}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower</td>
<td>2824.00</td>
<td>0.50</td>
<td>2822.00</td>
</tr>
<tr>
<td>Upper</td>
<td>2827.00</td>
<td>5.00</td>
<td>2823.50</td>
</tr>
<tr>
<td>Avg. 1</td>
<td>2824.74</td>
<td>2.39</td>
<td>2822.50</td>
</tr>
<tr>
<td>Std.</td>
<td>0.39</td>
<td>0.11</td>
<td>0.01</td>
</tr>
<tr>
<td>Avg. 2</td>
<td>2824.70</td>
<td>2.11</td>
<td>2822.51</td>
</tr>
<tr>
<td>Std.</td>
<td>0.35</td>
<td>0.09</td>
<td>0.00</td>
</tr>
<tr>
<td>Avg. 3</td>
<td>2824.72</td>
<td>2.09</td>
<td>2822.54</td>
</tr>
<tr>
<td>Std.</td>
<td>0.33</td>
<td>0.10</td>
<td>0.02</td>
</tr>
<tr>
<td>Avg. 4</td>
<td>2824.70</td>
<td>2.07</td>
<td>2822.52</td>
</tr>
<tr>
<td>Std.</td>
<td>0.37</td>
<td>0.12</td>
<td>0.01</td>
</tr>
<tr>
<td>Avg. 5</td>
<td>2824.66</td>
<td>2.09</td>
<td>2822.50</td>
</tr>
<tr>
<td>Std.</td>
<td>0.30</td>
<td>0.11</td>
<td>0.01</td>
</tr>
<tr>
<td>Avg. 6</td>
<td>2824.78</td>
<td>2.05</td>
<td>2822.51</td>
</tr>
<tr>
<td>Std.</td>
<td>0.43</td>
<td>0.14</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### Table 6.4
Fit results for relevant parameters corresponding to features in the Ru L-edge region of the Cl K- and Ru L_{2,3}-edges XAS data sets 1-6 for compound 1a.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{Ru}$ L_{3}/L_{2} (B1)</th>
<th>$I_{P3}$ (Ru-L_{2}) (normalised)</th>
<th>$E_{P3}$ (eV)</th>
<th>$I_{P4}$ (Ru-L_{2}) (normalised)</th>
<th>$E_{P4}$ (eV)</th>
<th>$E_{P4}-E_{P3}$ (eV)</th>
<th>$E_{P3}-E_{P3}$ (eV)</th>
<th>$\Delta (W_{2})$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower</td>
<td>1.50</td>
<td>5.00</td>
<td>2839.00</td>
<td>0.00</td>
<td>2.50</td>
<td>3.50</td>
<td>127.00</td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>2.00</td>
<td>15.00</td>
<td>2842.50</td>
<td>15.00</td>
<td>4.00</td>
<td>10.50</td>
<td>130.00</td>
<td></td>
</tr>
<tr>
<td>Avg. 1</td>
<td>1.73</td>
<td>11.79</td>
<td>2841.18</td>
<td>2.31</td>
<td>3.18</td>
<td>6.28</td>
<td>128.82</td>
<td></td>
</tr>
<tr>
<td>Std.</td>
<td>0.01</td>
<td>0.91</td>
<td>0.06</td>
<td>0.29</td>
<td>0.12</td>
<td>0.73</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Avg. 2</td>
<td>1.71</td>
<td>9.77</td>
<td>2840.98</td>
<td>1.68</td>
<td>3.71</td>
<td>6.99</td>
<td>128.81</td>
<td></td>
</tr>
<tr>
<td>Std.</td>
<td>0.08</td>
<td>2.03</td>
<td>0.18</td>
<td>0.88</td>
<td>0.23</td>
<td>0.70</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Avg. 3</td>
<td>1.61</td>
<td>10.96</td>
<td>2841.10</td>
<td>1.68</td>
<td>3.67</td>
<td>7.05</td>
<td>128.94</td>
<td></td>
</tr>
<tr>
<td>Std.</td>
<td>0.03</td>
<td>2.37</td>
<td>0.03</td>
<td>0.50</td>
<td>0.19</td>
<td>0.46</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Avg. 4</td>
<td>1.60</td>
<td>11.03</td>
<td>2841.05</td>
<td>1.64</td>
<td>3.74</td>
<td>7.00</td>
<td>128.94</td>
<td></td>
</tr>
<tr>
<td>Std.</td>
<td>0.05</td>
<td>2.26</td>
<td>0.09</td>
<td>0.45</td>
<td>0.15</td>
<td>0.54</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Avg. 5</td>
<td>1.63</td>
<td>10.57</td>
<td>2841.01</td>
<td>1.67</td>
<td>3.71</td>
<td>7.03</td>
<td>128.96</td>
<td></td>
</tr>
<tr>
<td>Std.</td>
<td>0.08</td>
<td>2.17</td>
<td>0.19</td>
<td>0.89</td>
<td>0.22</td>
<td>0.56</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Avg. 6</td>
<td>1.64</td>
<td>10.40</td>
<td>2841.06</td>
<td>1.55</td>
<td>3.70</td>
<td>6.79</td>
<td>128.94</td>
<td></td>
</tr>
<tr>
<td>Std.</td>
<td>0.03</td>
<td>1.72</td>
<td>0.09</td>
<td>0.38</td>
<td>0.17</td>
<td>0.49</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>
However, from Figure 6.5 (Page 203), samples 1-2 show markedly different intensity ratios between the Cl K- and Ru L-edges and between the Ru L\textsubscript{3}- and L\textsubscript{2}-edges, when compared with the data sets from samples 3-6. Additionally, the intensity of the pre-edge in the Cl K-edge region seems more intense in relation to its corresponding edge jump (Figure 6.5b), and the intensity and more importantly the shape of the second peak feature in the Ru L\textsubscript{3}-edge, shown in Figure 6.5c, is significantly different in the first two data sets compared with the rest.

As indicated in Table 6.2, samples 1 and 2 were not diluted with BN. Although at the time, the quality of these data (particularly the first data set) was considered remarkably good due to its sharp, intense features, the fit results summarised in Table 6.3 and Table 6.4 indicate that the observed differences between these data sets and those from diluted samples may be due to distortion effects in the concentrated samples. In this regard, the flattened top observed for the second feature in the Ru L\textsubscript{3}-edge of the first two data sets (Figure 6.5c) is a good indicator of the presence of self-absorption effects (137). Therefore, the results from data sets 1-2 were not considered further in this analysis.

As discussed in Section 2.4, the intensity of the normalised pre-edge feature in the Cl K-edge XAS spectrum directly reflects the amount of chlorine character in the empty low-lying molecular orbitals (Equation 2.5). In principle, the intensity of the pre-edge in the case of compounds 1\textit{a} should reflect the amount of chlorine into the Ru-4d based MOs, but other low-lying MOs based on \(\pi^*\)-back bonding ligands can also contain a significant amount of chlorine character and hence contribute to the intensity of the pre-edge.

The ground state calculations listed on Table 5.4\textit{a} (Page 174) for compound 1\textit{a} reveal that a total of 25% of chlorine is contained in the Ru-4d based empty MOs. These results also reveal a negligible amount of chlorine in the \(\pi^*\) back bonding carbene-based orbital. Experimentally, the pre-edge peak has an estimated normalised intensity (based on the fit results for data sets 3-6) of 2.07 ± 0.08. From previous studies (128) in D\textsubscript{4h} CuCl\textsubscript{4}\textsuperscript{2-}, a normalised pre-edge intensity of 0.76 in that complex correlates with a covalency value of 9.8% per chlorine atom per orbital. Therefore, the
pre-edge intensity for 1a corresponds to a total chlorine contribution of 26.7 ± 1.0%, which is in very good agreement with the DFT-calculated value.

Moreover, the results from time-dependent DFT and Slater ΔSCF calculations suggest that the transitions to the Ru-4d based empty MOs are the origin of the observed pre-edge. The optimised simulation in Figure 6.6 is obtained using a similar approach to the one discussed in section 4.4. From the energies and oscillator strengths for the 40 transition lines obtained, two band functions are created, one comprising the transitions exclusively to low-lying empty MOs (206 a₁- 208 a₁; Figure 5.15 [Page175]) and the other one comprising the rest of the transitions. Each of these functions depends on a common scaling factor that proportionally increases the intensity of all the lines, a common shift parameter that displaces by the same amount the lines, a single value to modulate the line shape (in terms of Gaussian fraction) in all the lines, and a modulating width function similar to that shown in Figure 4.11. The parameters in the band functions are then optimised in Blueprint XAS. A similar approach is taken to generate the optimised simulation of Figure 6.7. In this case, however, due to the amount of computational resources required to compute Slater ΔSCF corrections for all the 40 transition lines, only the lines corresponding to transitions to the low-lying empty MOs (also listed on Table 6.5) are considered.

**Table 6.5** Results for the time-dependent DFT calculation and Slater ΔSCF corrections in the energy for the Cl K-edge transitions involving the low-lying empty molecular orbitals of compound 1a.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>Energy</th>
<th>ΔSCF</th>
<th>Oscillator strength, f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₁₁(2 a₁)</td>
<td>π⁺_{Ru-C} (206 a₁)</td>
<td>2735.1</td>
<td>-0.28</td>
<td>1.88x10⁻⁵</td>
</tr>
<tr>
<td>Cl₁₁(1 a₁)</td>
<td>π⁺_{Ru-C} (206 a₁)</td>
<td>2735.2</td>
<td>-0.28</td>
<td>1.73 x10⁻⁵</td>
</tr>
<tr>
<td>Cl₁₁(2 a₁)</td>
<td>Ru-4dₓ⁺ (207 a₁)</td>
<td>2736.1</td>
<td>0</td>
<td>0.000656</td>
</tr>
<tr>
<td>Cl₁₁(1 a₁)</td>
<td>Ru-4dₓ⁺ (207 a₁)</td>
<td>2736.3</td>
<td>0</td>
<td>0.000619</td>
</tr>
<tr>
<td>Cl₁₁(2 a₁)</td>
<td>Ru-4dₓ⁺ (208 a₁)</td>
<td>2736.5</td>
<td>0.49</td>
<td>0.0007</td>
</tr>
<tr>
<td>Cl₁₁(1 a₁)</td>
<td>Ru-4dₓ⁺ (208 a₁)</td>
<td>2736.6</td>
<td>0.49</td>
<td>0.000683</td>
</tr>
</tbody>
</table>
Figure 6.6 (a) Optimised simulation fit to the Cl K-edge XAS spectrum of 1a, obtained from time-dependent DFT-calculation results. (b) Relative position of calculated transition lines to low-lying MOs in the optimised simulation fit.

Figure 6.7 (a) Optimised simulation fit to the Cl K-edge XAS spectrum of 1a, obtained from time-dependent DFT-calculation results including Slater ΔSCF energy corrections. (b) Relative position of calculated transition lines to low-lying MOs in the optimised simulation fit.
Second-generation Grubbs catalyst, 1b

Similar to the analysis of data sets in 1a, Figure 6.8 shows a representative example for the fitting of the data sets of 1b. Table 6.6 and Table 6.7 list relevant fitted parameters and Figure 6.9 displays the normalised Cl K- and Ru L_{2,3}-edges XAS data sets for compound 1b.

**Figure 6.8** Representative fit to a Cl K- and Ru L-edges XAS data set of compound 1b, showing the relevant components in the evaluation function in the region near (a) the Cl K-edge and (b) the Ru L_{3}-edge.
Figure 6.9 Normalised CI K- and Ru L\textsubscript{2,3}-edges XAS spectra for samples 1 (darker) - 4 (lighter) in compound \textit{1b}, showing (a) the region near the CI K-edge, (b) the region involving all spectral features and (c) the region near the Ru L-edge.

Figure 6.9 suggests that once more the two data sets collected from non-diluted samples 1 and 2 were subject to important distortion effects and are not considered further. Note however that the Ru L\textsubscript{3}/L\textsubscript{2} branching ratio on the first data set ($B_1 = 1.70 \pm 0.01$; Table 6.7) is in only somewhat close agreement with that previously reported ($\lambda_{\text{Ru} L\textsubscript{3}/L\textsubscript{2}}=1.74$;
The observed differences suggest that the results originally obtained for this parameter may have been slightly biased in compounds 1b, 2a and 2b (see also Table 6.9 and Table 6.11).

**Table 6.6** Fit results for relevant parameters corresponding to features in the Cl K-edge region of the Cl K- and Ru L_{2,3}-edges XAS data sets 1-4 for compound 1b.

<table>
<thead>
<tr>
<th></th>
<th>E_{e1} (eV)</th>
<th>I_{p1} (normalised)</th>
<th>E_{p1} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower</td>
<td>2824.00</td>
<td>0.50</td>
<td>2822.00</td>
</tr>
<tr>
<td>Upper</td>
<td>2827.00</td>
<td>5.00</td>
<td>2823.50</td>
</tr>
<tr>
<td>1 Avg.</td>
<td>2824.76</td>
<td>2.07</td>
<td>2822.51</td>
</tr>
<tr>
<td>Std.</td>
<td>0.51</td>
<td>0.15</td>
<td>0.01</td>
</tr>
<tr>
<td>2 Avg.</td>
<td>2824.69</td>
<td>2.21</td>
<td>2822.55</td>
</tr>
<tr>
<td>Std.</td>
<td>0.22</td>
<td>0.15</td>
<td>0.01</td>
</tr>
<tr>
<td>3 Avg.</td>
<td>2824.62</td>
<td>2.00</td>
<td>2822.57</td>
</tr>
<tr>
<td>Std.</td>
<td>0.35</td>
<td>0.20</td>
<td>0.01</td>
</tr>
<tr>
<td>4 Avg.</td>
<td>2824.72</td>
<td>1.96</td>
<td>2822.54</td>
</tr>
<tr>
<td>Std.</td>
<td>0.48</td>
<td>0.24</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Table 6.7** Fit results for relevant parameters corresponding to features in the Ru L-edge region of the Cl K- and Ru L_{2,3}-edges XAS data sets 1-4 for compound 1b.

<table>
<thead>
<tr>
<th></th>
<th>\lambda_{Ru} L_3/L_2 (B_1)</th>
<th>I_{p3} (Ru-L_2) (normalised)</th>
<th>E_{p3} (eV)</th>
<th>I_{p4} (Ru-L_2) (normalised)</th>
<th>E_{p4}-E_{p3} (eV)</th>
<th>E_{p5}-E_{p3} (eV)</th>
<th>\Delta (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower</td>
<td>1.50</td>
<td>5.00</td>
<td>2839.00</td>
<td>0.00</td>
<td>2.50</td>
<td>6.50</td>
<td>127.00</td>
</tr>
<tr>
<td>Upper</td>
<td>2.00</td>
<td>15.00</td>
<td>2842.50</td>
<td>15.00</td>
<td>4.00</td>
<td>16.00</td>
<td>130.00</td>
</tr>
<tr>
<td>1 Avg.</td>
<td>1.70</td>
<td>12.64</td>
<td>2841.40</td>
<td>4.03</td>
<td>2.64</td>
<td>9.76</td>
<td>128.86</td>
</tr>
<tr>
<td>Std.</td>
<td>0.01</td>
<td>0.86</td>
<td>0.06</td>
<td>0.34</td>
<td>0.06</td>
<td>0.56</td>
<td>0.00</td>
</tr>
<tr>
<td>2 Avg.</td>
<td>1.68</td>
<td>12.75</td>
<td>2841.34</td>
<td>2.77</td>
<td>2.82</td>
<td>10.12</td>
<td>128.75</td>
</tr>
<tr>
<td>Std.</td>
<td>0.02</td>
<td>0.98</td>
<td>0.09</td>
<td>0.54</td>
<td>0.11</td>
<td>0.32</td>
<td>0.01</td>
</tr>
<tr>
<td>3 Avg.</td>
<td>1.50</td>
<td>10.62</td>
<td>2841.17</td>
<td>1.37</td>
<td>3.50</td>
<td>9.29</td>
<td>128.94</td>
</tr>
<tr>
<td>Std.</td>
<td>0.04</td>
<td>1.35</td>
<td>0.09</td>
<td>0.34</td>
<td>0.16</td>
<td>0.59</td>
<td>0.02</td>
</tr>
<tr>
<td>4 Avg.</td>
<td>1.52</td>
<td>11.57</td>
<td>2841.14</td>
<td>1.75</td>
<td>3.44</td>
<td>9.33</td>
<td>128.94</td>
</tr>
<tr>
<td>Std.</td>
<td>0.06</td>
<td>1.37</td>
<td>0.22</td>
<td>1.54</td>
<td>0.20</td>
<td>0.65</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Furthermore, from the fit results on data sets 3-4, the normalised intensity of the pre-edge, with an estimated value of 1.98 ± 0.19, corresponds to a covalency of 25.5 ±
2.5% of chlorine contribution in the empty low-lying MOs of 1b, in very close agreement with the obtained covalency for 1a and in somewhat close agreement with the obtained results from ground-state DFT calculations (20%, Table 5.5a [Page 178]). The experimental results suggest similar Ru-Cl bond covalencies in both complexes and further support the idea that substitution of one of the PCy₃ ligands by an NHC does not significantly alter the bonding interactions with the rest of the ligands. Consistently, the comparison between the normalised spectrum for one of the data sets in 1a and 1b (Figure 6.10) reveals a very similar pre-edge intensity and a similar inflection point in the Cl K-edge jump. Moreover, the comparison around the Ru L₃-edge reveals a slight shift on the overall structure of the edge consistent with an increase of the charge in the metal centre. Contrary to the equivalent assertion in the analysis of the Ru K-edge XAS spectra for these two complexes, this overall observation in the Ru L-edge requires a more careful examination. The Ru L-edge is subject to important multiplet and electronic relaxation effects that can modify the relative position of the pre-edge features. However, the close agreement in relative intensity of their individual features and their shape around the Ru L₃-edge (Figure 6.10b) indicates similar ligand field and bonding interactions in both complexes.

As in the case of compound 1a, time-dependent DFT (Figure 6.11) and Slater ΔSCF energy corrections in compound 1b (Figure 6.12 and Table 6.8), suggest that the intensity of the pre-edge originates from the chlorine content into the Ru-4d based MOs. However, the time-dependent DFT calculation simulation of Figure 6.11 reveals that transitions to mainly the MO 214 a₁ (Figure 6.13) contribute significantly to the intensity of the pre-edge. Moreover, the ground state calculation results for 1b indicate that this orbital is closely related in nature to the MO 213 a₁ (Figure 5.18 [Page 179]) with a Cl-3p content of nearly 7%, a Ru-4d content of 26% and an NHC content of 49%. MO 214 a₁ is therefore an NHC-based orbital whose close proximity in energy and symmetry causes substantial adventitious mixing with MO 213 a₁. Considering the amount of chlorine-3p in MO 214 a₁, the accumulated chlorine-3p contribution into Ru-4d orbitals can be thought as of about 27% (20+7), which is in closer agreement with the experimentally obtained results. Furthermore, although the fact that the chlorine-3p content in the NHC-based π-back bonding orbital MO 219 a₁ is negligible (Table 5.5a
a considerable amount of chlorine character has been transferred to this orbital in the excited state, as suggested by the relatively high oscillator strength computed.

**Figure 6.10** Comparison between normalised Cl K- and Ru L2,3-edges data sets of 1a and 1b in the region near (a) the Cl K-edge and (b) the Ru L3-edge.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>Energy</th>
<th>ΔSCF</th>
<th>Oscillator strength, f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl1s (2 a1)</td>
<td>π*Ru=NC (219 a1)</td>
<td>2737.3</td>
<td>1.82</td>
<td>8.19 x10^{-5}</td>
</tr>
<tr>
<td>Cl1s (1 a1)</td>
<td>π*Ru=NC (219 a1)</td>
<td>2737.4</td>
<td>1.82</td>
<td>6.69 x10^{-5}</td>
</tr>
</tbody>
</table>
Figure 6.11  (a) Optimised simulation fit to the Cl K-edge XAS spectrum of 1b, obtained from time-dependent DFT-calculation results. (b) Relative position of calculated transition lines to low-lying MOs in the optimised simulation fit.

Figure 6.12  (a) Optimised simulation fit to the Cl K-edge XAS spectrum of 1b, obtained from time-dependent DFT-calculation results including Slater $\Delta$SCF energy corrections. (b) Relative position of calculated transition lines to low-lying MOs in the optimised simulation fit.
**Results on Piers first- and second-generation analogues**

The Cl K-edge region of the Cl K- and Ru L\textsubscript{2,3}-edges XAS spectra for 2\textit{a} and 2\textit{b} exhibit additional features in the pre-edge region (see Figure 6.14 and Figure 6.16). In Piers analogues, ground-state DFT calculations reveal that an important contribution to the intensity of the pre-edge should come from a transition to the $\pi$-back bonding carbene-based MO, which was not observed in the Grubbs analogues. This is because the $\pi$–system with the carbene in the Grubbs analogues is rotated $\sim$90 degrees with respect to the $\pi$-system in compounds 2\textit{a} and 2\textit{b}. Consequently, the Ru-4d orbital interacting with the corresponding $\pi$-bonding system is different and inaccessible for the interaction with the chlorine atoms in the case of the Grubbs analogues (compare, for example, MO 206 \textit{a}\textsubscript{1} in Figure 5.15 [Page 175] with MO 185 \textit{a}\textsubscript{1} in Figure 5.16 [Page 176]).

From Table 6.9, the total normalised intensity of the pre-edge in 2\textit{a} (excluding only the first data set; see Figure 6.15) is estimated as 2.73 ± 0.23, corresponding to a covalency value equivalent to 35.2 ± 3.0% of chlorine-3p character, which is in good agreement with DFT calculations from which a total of 39% of Cl-3p is obtained in the
low-lying MOs (Table 5.5b [Page 178]). From Table 6.11, on the other hand, the total normalised intensity for 2b is estimated (excluding data sets 1 and 4; see Figure 6.17) as $2.46 \pm 0.35$, which is equivalent to a covalency of $31.7 \pm 4.6\%$, which is somewhat in disagreement with DFT results from which a 39 % of Cl-3p character is obtained (Table 5.4b [Page 174]).

**Figure 6.14** Representative fit to a Cl K- and Ru L-edges XAS data set of compound 2a, showing the relevant components in the evaluation function in the region near (a) the Cl K-edge and (b) the Ru L$_3$-edge.

Time-dependent DFT and Slater $\Delta$SCF simulation fits also suggest a significant amount of intensity to the carbene-based MO. The Slater $\Delta$SCF fits of Figure 6.19 and Figure 6.21 support the idea that the main feature observed in the pre-edge region of
the Cl K-edge XAS of 2a and 2b is due to transitions to the carbene-based MOs and to transitions to the Ru-4d based MOs oriented mostly in the direction of the chlorine atoms (MO 186 a1 in Figure 5.16 (Page 176) and MO 191 a1 in Figure 5.19 (Page 180), respectively). These computations also suggest that the shoulder is due to transitions to the other Ru-4d based empty MO.

**Figure 6.15** Normalised Cl K- and Ru L_{2,3}-edges XAS spectra for samples 1 (darker) - 6 (lighter) in compound 2a, showing (a) the region near the Cl K-edge, (b) the region involving all spectral features and (c) the region near the Ru L-edge.
### Table 6.9

Fit results for relevant parameters corresponding to features in the Cl K-edge region of the Cl K- and Ru L_{2,3}-edges XAS data sets 1-6 for compound 2a.

<table>
<thead>
<tr>
<th></th>
<th>$E_{e1}$ (eV)</th>
<th>$I_{P1}$ (normalised)</th>
<th>$E_{P1}$ (eV)</th>
<th>$I_{P2}$ (normalised)</th>
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<tr>
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<td>2821.89</td>
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<td>0.02</td>
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<td>Avg.</td>
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<tr>
<td>Std.</td>
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<td>0.01</td>
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<tr>
<td>Std.</td>
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<td>0.01</td>
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<td>2822.50</td>
<td>5.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Avg.</td>
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<td>2821.89</td>
<td>0.62</td>
<td>1.18</td>
</tr>
<tr>
<td>Std.</td>
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<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>1.09</td>
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<th>$I_{P1}$ (normalised)</th>
<th>$E_{P1}$ (eV)</th>
<th>$I_{P2}$ (normalised)</th>
<th>$E_{P2}-E_{P1}$ (eV)</th>
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<td>2821.50</td>
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<td>0.50</td>
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<tr>
<td>Upper</td>
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<td>2822.50</td>
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<td>2.00</td>
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<tr>
<td>Avg.</td>
<td>2826.25</td>
<td>1.99</td>
<td>2821.89</td>
<td>0.62</td>
<td>1.18</td>
</tr>
<tr>
<td>Std.</td>
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<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>1.09</td>
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### Table 6.10

Fit results for relevant parameters corresponding to features in the Ru L-edge region of the Cl K- and Ru L_{2,3}-edges XAS data sets 1-4 for compound 2a.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{Ru} L_2/L_1$ (Bf)</th>
<th>$I_{P5}(Ru-L_2)$ (normalised)</th>
<th>$E_{P4}$ (eV)</th>
<th>$I_{P5}(Ru-L_2)$ (normalised)</th>
<th>$E_{P5}-E_{P4}$ (eV)</th>
<th>$E_{P6}-E_{P4}$ (eV)</th>
<th>$\Delta$ (eV)</th>
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<tbody>
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<td>5.00</td>
<td>2839.00</td>
<td>0.00</td>
<td>3.00</td>
<td>5.50</td>
<td>127.00</td>
</tr>
<tr>
<td>Upper</td>
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<td>18.00</td>
<td>2842.50</td>
<td>7.20</td>
<td>4.50</td>
<td>12.00</td>
<td>130.00</td>
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<td>128.75</td>
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<td>0.02</td>
<td>0.14</td>
<td>0.18</td>
<td>0.45</td>
<td>0.01</td>
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<tr>
<td>1</td>
<td>Avg.</td>
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<td>2841.21</td>
<td>0.50</td>
<td>4.45</td>
<td>8.26</td>
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<tr>
<td>Std.</td>
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<td>0.02</td>
<td>0.37</td>
<td>0.29</td>
<td>0.38</td>
<td>0.02</td>
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<td>8.57</td>
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<td>1.76</td>
<td>0.02</td>
<td>0.29</td>
<td>0.48</td>
<td>0.17</td>
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</tr>
<tr>
<td>3</td>
<td>Avg.</td>
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<td>12.83</td>
<td>2841.19</td>
<td>0.60</td>
<td>4.35</td>
<td>8.37</td>
</tr>
<tr>
<td>Std.</td>
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<td>1.65</td>
<td>0.01</td>
<td>0.29</td>
<td>0.47</td>
<td>0.18</td>
<td>0.01</td>
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<td>4</td>
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<tr>
<td>Std.</td>
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<td>1.77</td>
<td>0.01</td>
<td>0.19</td>
<td>0.35</td>
<td>0.19</td>
<td>0.01</td>
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<tr>
<td>5</td>
<td>Avg.</td>
<td>1.61</td>
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<td>2841.18</td>
<td>0.51</td>
<td>4.41</td>
<td>8.33</td>
</tr>
<tr>
<td>Std.</td>
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<td>1.58</td>
<td>0.02</td>
<td>0.40</td>
<td>0.56</td>
<td>0.50</td>
<td>0.01</td>
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</table>
Figure 6.16  Representative fit to a Cl K- and Ru L-edges XAS data set of compound 2b, showing the relevant components in the evaluation function in the region near (a) the Cl K-edge and (b) the Ru L3-edge.

Figure 6.17  Normalised Cl K- and Ru L2,3-edges XAS spectra for samples 1 (darker) - 4 (lighter) in compound 2b, showing (a) the region near the Cl K-edge, (b) the region involving all spectral features and (c) the region near the Ru L-edge.
Table 6.11  Fit results for relevant parameters corresponding to features in the Cl K-edge region of the Cl K- and Ru L_{2,3}-edges XAS data sets 1-6 for compound 2b.

<table>
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<tr>
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<th>$E_{e1}$ (eV)</th>
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<th>$E_{P1}$ (eV)</th>
<th>$I_{P2}$ (normalised)</th>
<th>$E_{P2} - E_{P1}$ (eV)</th>
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<td>0.50</td>
</tr>
<tr>
<td>Upper</td>
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<td>5.00</td>
<td>2822.50</td>
<td>5.00</td>
<td>2.00</td>
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<tr>
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<td>2822.05</td>
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<td>0.97</td>
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<td>2821.97</td>
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<td>Avg.</td>
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<td>0.97</td>
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<tr>
<td>Avg.</td>
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<td>2822.01</td>
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<td>0.97</td>
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<td>Std.</td>
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<td>0.21</td>
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Table 6.12  Fit results for relevant parameters corresponding to features in the Ru L-edge region of the Cl K- and Ru L_{2,3}-edges XAS data sets 1-4 for compound 2b.

<table>
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<tr>
<th></th>
<th>$\lambda_{Ru L_3/L_2}$ (B₁)</th>
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<th>$E_{P4}$ (eV)</th>
<th>$I_{P5}$ (Ru-L₂) (normalised)</th>
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<th>$\Delta$ (eV)</th>
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<tbody>
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<td>Lower</td>
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<td>2842.50</td>
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<td>3.50</td>
<td>12.00</td>
</tr>
<tr>
<td>Avg.</td>
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<td>11.05</td>
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<td>11.16</td>
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<td>9.31</td>
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<tr>
<td>Std.</td>
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<td>3.43</td>
<td>0.22</td>
<td>3.78</td>
<td>0.68</td>
<td>0.93</td>
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Experimentally, the difference between these two features corresponds to an energy of $1.10\pm0.06$ eV (from Table 6.9) in 2a; and to an energy of $0.98 \pm 0.12$ eV (from Table 6.11) in 2b. This implies large splittings and/or large differences in electronic relaxation effects between the two Ru-4d based orbitals. From ground-state DFT calculations, the difference in energy between these two orbitals is only 0.45 eV in 2a (Table 5.4b [Page 174]) and 0.35 eV in 2b (Table 5.5b [Page 178]).
Figure 6.18 (a) Optimised simulation fit to the Cl K-edge XAS spectrum of 2a, obtained from time-dependent DFT-calculation results. (b) Relative position of calculated transition lines to low-lying MOs in the optimised simulation fit.

Figure 6.19 (a) Optimised simulation fit to the Cl K-edge XAS spectrum of 2a, obtained from time-dependent DFT-calculation results including Slater $\Delta$SCF energy corrections. (b) Relative position of calculated transition lines to low-lying MOs in the optimised simulation fit.
Figure 6.20 (a) Optimised simulation fit to the Cl K-edge XAS spectrum of 2b, obtained from time-dependent DFT-calculation results. (b) Relative position of calculated transition lines to low-lying MOs in the optimised simulation fit.

Figure 6.21 (a) Optimised simulation fit to the Cl K-edge XAS spectrum of 2b, obtained from time-dependent DFT-calculation results including Slater ∆SCF energy corrections. (b) Relative position of calculated transition lines to low-lying MOs in the optimised simulation fit.
Table 6.13  Results for the time-dependent DFT calculation and Slater $\Delta$SCF energy corrections for the Cl K-edge transitions to the low-lying empty molecular orbitals in compound 2a.

<table>
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<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>Energy</th>
<th>$\Delta$SCF</th>
<th>Oscillator strength, $f$</th>
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<tr>
<td>Cl$_{1s}$ (2a$_1$)</td>
<td>$\pi^*_{Ru=C}$ (185a$_1$)</td>
<td>2735.8</td>
<td>-0.19</td>
<td>0.000558</td>
</tr>
<tr>
<td>Cl$_{1s}$ (1a$_1$)</td>
<td>$\pi^*_{Ru=C}$ (185a$_1$)</td>
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<td>-0.19</td>
<td>0.000507</td>
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<td>Cl$_{1s}$ (2a$_1$)</td>
<td>Ru 4d$_{o^*}$ (186a$_1$)</td>
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<tr>
<td>Cl$_{1s}$ (1a$_1$)</td>
<td>Ru 4d$_{o^*}$ (186a$_1$)</td>
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<td>0.001269</td>
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<tr>
<td>Cl$_{1s}$ (2a$_1$)</td>
<td>Ru 4d$_{o^*}$ (187a$_1$)</td>
<td>2736.6</td>
<td>0.78</td>
<td>0.000265</td>
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<tr>
<td>Cl$_{1s}$ (1a$_1$)</td>
<td>Ru 4d$_{o^*}$ (187a$_1$)</td>
<td>2736.6</td>
<td>0.78</td>
<td>0.000332</td>
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</table>

Table 6.14  Results for the time-dependent DFT calculation and Slater $\Delta$SCF energy corrections for the Cl K-edge transitions to the low-lying empty molecular orbitals in compound 2b.

<table>
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<th>Donor</th>
<th>Acceptor</th>
<th>Energy</th>
<th>$\Delta$SCF</th>
<th>Oscillator strength, $f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_{1s}$ (2a$_1$)</td>
<td>$\pi^*_{Ru=C}$ (190 a$_1$)</td>
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<tr>
<td>Cl$_{1s}$ (1a$_1$)</td>
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<td>0.000514</td>
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<tr>
<td>Cl$_{1s}$ (2a$_1$)</td>
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<td>0</td>
<td>0.001385</td>
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<tr>
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<tr>
<td>Cl$_{1s}$ (2a$_1$)</td>
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<td>0.000271</td>
</tr>
<tr>
<td>Cl$_{1s}$ (1a$_1$)</td>
<td>Ru 4d$_{o^*}$ (192 a$_1$)</td>
<td>2736.6</td>
<td>0.81</td>
<td>0.000265</td>
</tr>
<tr>
<td>Cl$_{1s}$ (2a$_1$)</td>
<td>$\pi^*_{RuNHC}$ (195 a$_1$)</td>
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<td>3.37x10$^{-5}$</td>
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<tr>
<td>Cl$_{1s}$ (1a$_1$)</td>
<td>$\pi^*_{RuNHC}$ (195 a$_1$)</td>
<td>2738</td>
<td>2.69</td>
<td>0.000118</td>
</tr>
</tbody>
</table>

Including electronic relaxation effects, the difference between the two corresponding transition lines (as obtained from Slater $\Delta$SCF calculations) is $\sim$0.78 eV for 2a (Table 6.13) and $\sim$0.81 eV for 2b (Table 6.14), which are in better agreement with the obtained experimental values. A possible rationale for the source of the large splitting between the two transition lines in the Slater $\Delta$SCF calculations is that only one of the Ru-4d orbitals is significantly rich in chlorine-3p content (25% in MO 186 a$_1$ compared with 4% in MO 187 a$_1$ for 2a; and 26% in MO 191 a$_1$ compared with 3% in
MO 192 a₁ for 2b). Therefore, only one of these orbitals becomes significantly more sensitive to shifts in energy (with respect to the other) as a core electron in the chlorine atom is created.

An alternative assignment that cannot be dismissed, however, is one in which the main feature is attributed to transitions to the Ru-4d based empty MOs and the shoulder peak to the transition to the carbene-based MO. From fit results listed in Table 6.9 and Table 6.11, it is evident that the intensity of the shoulder represents approximately a quarter (or less) of the intensity of the main feature. Since the chlorine content in a carbene-based MO should be less (due to the fact that chlorine atoms are not directly linked to carbene), it is therefore appealing to consider a smaller splitting between the two Ru-4d based orbitals and to attribute the shoulder to the transition to the carbene-based MO (see Figure 6.22).

The definitive assignment of this shoulder is of great importance since these two possibilities would involve a LUMO of a completely different nature, an important piece of information in this puzzle when trying to understand from where the reactivity of these complexes originates (see Chapter 7).

A summary of the results obtained for the experimental and DFT-calculated covalency in compounds 1 and 2 is given in Table 6.15. From this table, when exploring the two possible scenarios for the assignment of the peaks to the different MOs, it is worth noticing that the alternative assignment is in very good agreement with respect to the results obtained for the first peak. Therefore, if this view is correct, these results would imply that ground-state DFT calculations (including the results for 1a and 1b) are predicting correctly the Cl-3p content in the two Ru-4d based MOs, but are doing a poor job when predicting the results (Cl-3p content and relative energy) for the carbene-based MOs. A conclusive answer for this will require further investigation.

In addition, the difference in the experimental total covalency for complexes 2a and 2b is also evident from Figure 6.23, which shows a slightly weaker pre-edge 2b, although with a more or less constant shoulder peak. Moreover, the Ru L₃-edge for 2a and 2b in Figure 6.23b shows significant differences in the shape and the intensity of
the different features, which indicates a slightly different overall bonding structure between the two complexes.

**Figure 6.22** Possible assignments for pre-edge features in the Cl K-edge XAS spectrum of Piers analogues: (a) The main feature is attributed to transitions to one of the Ru-4d_σ* MOs (the one containing the largest quantity of chlorine) and to the carbene-based MO. The shoulder, about 1 eV above, is attributed to the transition to the other Ru-4d_σ* MO. (b) alternatively, the main feature is attributed to transitions to both of the Ru-4d_σ* MOs, whereas the shoulder is attributed to transitions to the carbene-based MO.

These results reveal that, for the four-coordinate Piers analogues, substitution of a phosphine ligand by an NHC has a greater impact on the remaining bonding interactions, and that a more positive ruthenium centre in 2b may be in part due to these overall bonding changes.
Figure 6.23 Comparison between normalised Cl K- and Ru L_{2,3}-edges data sets of compounds 2a and 2b in (a) the region near the Cl K-edge and (b) the region near the Ru L_{3}-edge.

![Comparison between normalised Cl K- and Ru L_{2,3}-edges data sets](image)

Table 6.15 Summary of results on the Ru-Cl covalency for compounds 1 and 2 in terms of the Cl-3p contributions to low-lying empty MOs.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Experimental Peak</th>
<th>Cl-3p contribution</th>
<th>DFT-Calculated^A</th>
<th>DFT-Calculated^B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Low-lying Empty MOs</td>
<td>Cl-3p Contribution</td>
</tr>
<tr>
<td>1a</td>
<td>f_{p1}</td>
<td>26.7 ± 1.0 %</td>
<td>207 a_{1v}, 208 a_{1}</td>
<td>25 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>212 a_{1v}, 213 a_{1} (+ 214 a_{1})</td>
<td>27 %</td>
</tr>
<tr>
<td>1b</td>
<td>f_{p1}</td>
<td>25.5 ± 2.5 %</td>
<td>185 a_{1v}, 186 a_{1}</td>
<td>35 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>187 a_{1}</td>
<td>4 %</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>35.2 ± 3.0 %</td>
<td>Total</td>
<td>39 %</td>
</tr>
<tr>
<td>2a</td>
<td>f_{p1}</td>
<td>28.2 ± 1.7 %</td>
<td>190 a_{1v}, 191 a_{1}</td>
<td>36 %</td>
</tr>
<tr>
<td></td>
<td>f_{p2}</td>
<td>7.0 ± 1.3 %</td>
<td>192 a_{1}</td>
<td>3 %</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>31.7 ± 4.6 %</td>
<td>Total</td>
<td>39 %</td>
</tr>
</tbody>
</table>

A. From ground-state DFT calculation results listed in Table 5.4 and Table 5.5
B. Alternative MO assignment in compounds 2a and 2b (see Figure 6.22)
6.1.4. Multiplet simulations and the Ru L-edge

The analysis of metal L-edge XAS is accomplished through multiplet simulations, traditionally performed using variations to the Cowan programs and collectively termed recently as CTM4XAS (213). While this program was suitable for analysing data obtained from the available technology at the time, new ideas and techniques developed recently in the field require more sophisticated tools. For example, the recent ideas about probing $\pi$-back bonding in metal complexes (135) or the extraction of differential orbital covalency (139) from metal L-edge XAS have been performed using this program, but with important limitations and using 'tricks' to circumvent limitations in both the software and the model. One of the main reasons for this lies in the fact that, since the original code was written to account for atomic interactions in metal complexes, the basis set for the multiplets is expressed in terms of good quantum numbers within the weak-field representation.

However, quantities such as differential orbital covalency are easier to evaluate if the interaction matrices are worked out from a strong-field representation, under which the ligand-field and the VBCI interactions are the principal actors.

Very recently, I have developed a covalency and ligand-field multiplet simulator suite, named CoLoMoS for the moment, for the evaluation of differential orbital covalency in XAS. At this stage, the program can predict the ligand-field and VBCI multiplet structure of the ground and excited states as well as the intensities and energies for the possible transition lines in the metal L-edges XAS spectrum of a metal complex in a particular symmetry and subjected to different $\sigma$ and $\pi$ interactions. In this program, any number of metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT) states can be included to the ground and excited states to account for the different bonding interactions. This contrasts with the Cowan programs which were only recently modified to support the simultaneous incorporation of a single MLCT with a single LMCT state (135). Furthermore, while the Cowan programs compute the ground and excited states using the same ligand-field and the same VBCI off-diagonal parameter $T$ (Equation 4.5), CoLoMoS can compute the multiplets using a different set of parameters for the ground and excited states.
The output provides the intensity and energy for the transition lines classified as transitions to specific metal-based orbitals or to $\pi$-back bonding-based orbitals, allowing for a direct evaluation of differential orbital covalency. Additional information such as the ground-state wave function is also provided.

Ignoring atomic interactions, which have not been yet implemented in CoLoMoS, the applicability of this program is illustrated using the Ru L$_3$-edge XAS spectrum for compound 4a. The Ru L$_3$-edge XAS spectrum in compounds 4-7 is interesting because it exhibits two somewhat resolved features with about the same intensity in the pre-edge region, which can be attributed, as a reasonable first approximation, to transitions to the two Ru-4d based MOs of this compound. Ground-state DFT calculations for compounds 4-5 are in agreement with this assignment and predict a large splitting between these two orbitals in compounds 4 and 5. In addition to these features, the Ru L$_3$-edge for 4a also shows a small feature that can be attributed to transitions to charge transfer states. In any case, due to strong interactions with the six ligands in 4a, the Ru L-edge of XAS should be dominated by ligand-field and bonding interactions and not as significantly by atomic interactions in the metal.

To set up the simulation, the symmetry of compound 4a is established as $D_{4h}$. Based on the ground-state DFT calculation results for this compound (Figure 5.21 [Page 183] and Table 5.6 [Page 182]), MO 167 is assigned $b_2$ symmetry, MOs 168 and 169 are assigned $e$ symmetry, MO 173 is assigned $a_1$ symmetry, and finally MO 177 is assigned $b_1$ symmetry. Based on the splitting pattern of these orbitals in Figure 5.21, the parameter 10Dq is set as 4 eV. Moreover, to account for the differences between orbitals $a_1$ and $b_1$, the distortion parameters Ds and Dt were set as 0 eV and -0.3 eV, respectively. For simplicity, these parameters were set as the same for both the ground and excited states.

Regarding the VBCI parameters, according to Figure 5.21, the energy of the different atomic/fragment orbitals is used to roughly estimate the energy of the charge transfer states in the ground and excited states. For instance, the C-2p based orbital in the alkylidene fragment is about 0.5 eV above the energy of the ruthenium 4d shell. Therefore, a first MLCT state that accounts for the interaction of the C-2p orbital in the
alkylidene with the b_2 orbital in ruthenium is set up at about \Delta_1 = 0.5 eV, with reference on the energy of the pure-metal configuration. As the core hole is created in the excited state, however, the relative energies between these two energies should increase due to contraction of the ruthenium-based orbitals. Therefore, with reference to the pure-metal configuration of the excited state, the energy of the MLCT state is set up at about 0.8 eV.

Following the same approach and based on the MO diagram of Figure 5.21 (Page 183), the scheme of Figure 6.24 is obtained when also considering the mixing with MLCT states to account for the \pi-backbonding interaction with the pyridine ligands, and mixing with the LMCT state to account for the \sigma-bonding interaction with the chlorine atoms. The complete set of parameters used in the simulation and the respective values are listed in Table 6.16.

Based on the parameters given in Table 6.16, Figure 6.25 shows the simulated transition lines along with the best fit to the experimental Ru L_3-edge XAS data of 4a (light-grey dotted line). Moreover, in Table 6.17 the main basis set multiplet components of the ground-state wave function are given.

According to the output, the intensity of the a_1 band (comprising all the transitions with a_1 symmetry) has a total intensity of 1.84, compared with 1.99 in the b_1 band. These intensities reflect directly the covalency of each orbital in terms of their relative ruthenium-4d content. For orbital a_1, the reduction of 0.16 with respect to the regular value of 2.00 is well correlated with the contribution of the second component in the ground-state wavefunction, which indicates that 0.16 electrons have been transferred from the chlorine atoms to the a_1 orbital and that less room is available in that orbital for the Ru-2p core electrons.

Additionally, the output of this simulation also reveals that an amount equivalent to an intensity of 0.02 has been "borrowed" from the main a_1 transition line to lines that correspond to MLCT states and that an intensity of 0.18 has been borrowed from the b_1 main transition line to the lines in the MLCT states. Therefore, the effective intensity of a_1 is 1.82 and the one for b_1 is 1.81, whereas the intensity for the transition to the MLCT states corresponding to the carbene-based \pi-backbonding orbital is 0.16, and
that for the transition to the MLCT states corresponding to the pyridine-based $\pi$-backbonding orbitals is 0.02 each.

**Figure 6.24** Scheme used in the multiplet simulation of the Ru L$_3$-edge XAS spectrum of compound 4a.

While the fit and the simulation itself do not fit the experimental data very well, this example is useful to illustrate the potential of this model, as implemented in CoLoMoS. It is worth noticing that this simulation is the result of just a single trial with parameters that may not be very accurate, particularly in the case of the $T$ parameters. As stated before, the Cowan programs use the same value in the ground and excited states for the same kind of off-diagonal coupling. However, from the few simulations that have been tested in CoLoMoS, it has been noted that larger amounts of intensity can be borrowed when the difference between the $T$ values in the ground and excited states is larger. The rationale used here to justify the use of different values of $T$ has to do with the changes in the electronic structure after the core hole in the ruthenium 2p-shell is created. Since ruthenium orbitals are closer to the nucleus in the excited state, the
interaction with MLCT states should be reduced whereas the interaction with LMCT states is increased. While these measures seem to be reasonable, the full significance of different values of T and their magnitude need to be further investigated to be able to predict better starting values of future simulations.

**Table 6.16** List of parameters used in the multiplet simulation of the Ru L3-edge XAS of compound 4a.

<table>
<thead>
<tr>
<th>Parameters (eV)</th>
<th>Ground State</th>
<th>Excited State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Energy</td>
<td>0.0</td>
<td>2839.9</td>
</tr>
<tr>
<td>D4h - Ligand Field</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Dq</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Ds</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Dt</td>
<td>-0.3</td>
<td>-0.3</td>
</tr>
<tr>
<td>VBCI Parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MLCT - C (b2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta_1/\Delta_1^* )</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>( T_{b2}/T_{b2} )</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>LMCT - Cl (a1, b1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta_2/\Delta_2^* )</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>( T_{a1}/T_{a1} )</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>( T_{b1}/T_{b1} )</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>MLCT - py (e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta_3/\Delta_3^* )</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>( T_{\epsilon}/T_{\epsilon} )</td>
<td>0.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Table 6.17** Ground-state wave function and its principal basis set multiplet components in the simulation of the Ru L3-edge XAS spectrum of compound 4a.

<table>
<thead>
<tr>
<th>Component</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) (</td>
<td>e^4b_2^2\rangle )</td>
</tr>
<tr>
<td>(2) (</td>
<td>(e^4b_2^2a_1^\dagger)Cl_{a_1}^\dagger\rangle )</td>
</tr>
<tr>
<td>(3) (</td>
<td>(e^4b_1^\dagger)C_{b_1}^\dagger\rangle )</td>
</tr>
<tr>
<td>(4) (</td>
<td>(e^3b_2^2)py_{\epsilon}^\dagger\rangle )</td>
</tr>
</tbody>
</table>
Figure 6.25 Multiplet simulation (sticks) and fit (solid line) to the experimental Ru L₂₃-edge XAS data in compound 4a, displaying also the individual bands comprising transition lines with \( a_1 \) symmetry (blue) and \( b_1 \) symmetry (red).

6.2. C K-edge XAS data

During the last five years, additional data has been successfully collected on compounds 1-7 in the C K-edge region.

C K-edge region lies in the region of the soft X-rays, around energies where basically every element (including air and other inert gases) has a large photoionisation cross section. Therefore, a chamber under ultra-vacuum conditions is required, as described in Section 2.6.3. Furthermore, the detector used to collect this data (a channeltron) requires the sample to be placed over conducting surfaces. Typically, as the samples normally analysed under these conditions are first row transition metals, the samples are spread over carbon tape, a semiconductor material and a possible
interference in C K-edge experiments. After several attempts with conducting surfaces, such as silicon wafers and indium metal, the conducting material for which the best data can be collected was determined to be carbon tape.

Figure 6.26 shows the data sets as obtained for compounds 1-4. Additionally, Figure 6.27 shows the collected data on compounds 4-7. In both cases, the spectrum for carbon-tape is included for reference.

**Figure 6.26** C K-edge XAS spectra for samples of compounds 1-4 spread over carbon tape (C) in (a) the full scanned region and (b) the pre-edge region.
As is evident from these figures, the carbon tape interferes with the spectra in the near-edge and EXAFS regions but not in the pre-edge, the region of interest where the transitions to the low-lying empty MOs occur. The fact that the region above ~287 eV, where the edge jump should appear, contains only a small trace of the rising edge is due not to the carbon tape, which exhibits the same pattern, but to the protective diamond window in the UHV chamber (Figure 2.16). Above ~287 eV, the C-C $\sigma^*$ orbitals of diamond absorb most of the incident radiation before it reaches the sample. Furthermore, the small double well observed in the spectrum corresponding to the carbon tape is due to an abrupt change in intensity of the incident radiation around 284 eV, most probably due to the absorption of graphite in many of the components of
beamline 10-1 itself or inside the UHV chamber. Around that region, the spectra of the samples of every compound seem to be affected to different degrees, but without drastically changing their overall spectral structure.

Despite the technical difficulties, several common features can be identified. For example, the most intense peak feature just above 284 eV, only present in the second generation analogues, is very likely due to the transition to the \( \pi \)-back-bonding NHC-based MO. Also noticeable are the small peak features present in all spectra at about 282.5 and 283 eV, possibly due to transitions to the Ru-4d based MOs, and in the first-generation analogues, a more intense feature slightly above or below the region where the transitions to the NHC-based MO appears in the second-generation analogues. This latter feature might be due to transitions to the \( \pi \)-back-bonding carbene-based MOs. The only possible exception is for 1a, in which this feature appears to be smaller than the features suspected to be due to transitions to Ru-4d orbitals. These preliminary assignments support the idea that Ru-4d based orbitals may be lying below the carbene-based MOs (consistent with the alternative assignment of Figure 6.22b). The relative intensity of these pre-assigned features are also consistent with the carbene and NHC contributions predicted from the ground-state DFT calculations with results listed in Table 5.4-Table 5.7 (Pages 174,178,182 and 185) for compounds 1-5. From these results, it is worth noting that the major contributions are predicted for the \( \pi^*_{\text{Ru=C}} \) and \( \pi^*_{\text{RuNHC}} \) MOs, with smaller carbene or NHC contributions in the Ru-4d based MOs.

As opposed to Cl K-edge XAS, where transitions originate from only two atoms, in C K-edge XAS, the transitions originate from a larger number of carbon atoms present in each compound. Therefore, these tentative assignments need to be investigated further with the help of time-dependent DFT and Slater \( \triangle \)SCF computations.

It is also evident that the data displayed in Figure 6.26 and Figure 6.27 need to be processed differently than traditional XAS data sets to undergo normalisation procedures since there is really no clear edge-jump. A rough attempt to do so, while preparing these figures, was to normalise the data using the maximum intensity of the main feature below 287 eV (attributed to C-C \( \pi^* \) orbitals in the graphite of carbon tape).
Nevertheless, more effective approaches need to be developed to treat these particular data sets.

In a more recent trip to SSRL in 2008, the safety window in the UHV chamber was changed for an aluminium window to avoid the attenuation of the edge jump in the data. Additionally, a new sample holder with small wells was designed (Figure 6.28) and then fabricated from aluminium in the mechanical shop of the chemistry department of UBC.

**Figure 6.28** New design for the sample holder used during the collection of C K-edge XAS data during the 2008 trip to SSRL.

Using this new sample holder, instead of spreading the samples over carbon-tape, a small amount of compound was put inside the well together with 1-5 μL of toluene. The solid was dissolved and the resulting solution spread evenly inside the well. Upon evaporation of the toluene, a thin film of the compound was left behind.
Following this procedure, the C K-edge XAS spectra for compounds 1-3 and 6 (excluding compound 1b) have been successfully obtained and illustrated in Figure 6.29. Additional scans were taken for empty sample holders, which were cleaned in an ultrasonic machine operating with hot water for about an hour. A representative scan for an empty aluminium sample holder is also displayed in Figure 6.29.

**Figure 6.29** C K-edge XAS spectra for samples of compounds 1-3 and 6 evaporated from toluene over new aluminum sample holders (Al) in (a) the full scanned region and (b) the pre-edge region.

From this figure, it is evident that the pre-edge is more intense, relative to the edge jump, although the resolution of the features in some of the data sets is somewhat attenuated. Furthermore, the major peak assigned in Figure 6.27 as the transition to the carbene-based MOs is better-defined now in the first-generation
analogues, particularly in the case of 1a, for which a very intense peak around the same region as in the other complexes is observed.

The great potential of C K-edge XAS spectroscopy resides in the good resolution of the observed pre-edge features, permitting the direct evaluation of the relative carbon-2p content in the different low-lying empty MOs. Of particular interest, in this regard, is to probe \( \pi \) contributions from the NHC ligands and to further investigate the nature of the LUMO orbital in these compounds. Hence, the full development of the technique and the methodology to process C K-edge XAS data should provide very valuable insights into the electronic structure of ruthenium-based catalysts, olefin-metathesis intermediates and related species.
CHAPTER 7: CONCLUSIONS, FUTURE WORK AND RECOMMENDATIONS

Various X-ray spectroscopic techniques have been employed to investigate the electronic structure of ruthenium-based catalysts 1-7 relevant to the olefin metathesis reaction. Specific issues in the obtained data made necessary the development of new methodologies and tools to properly perform the analysis of these data. Computational methods were essential in the rationalisation of some of these results.

Blueprint XAS is the primary tool that was developed and used in the analysis of the Cl K-edge and Ru L\textsubscript{2,3}-edge XAS data. Its novel Monte-Carlo-based method for generating starting points permitted the generation of a large family of independent fits useful to investigate the robustness of fit models, to estimate errors in the evaluated parameters of the model, and to evaluate distortion effects in the data. Additional Matlab-based codes used in conjunction with Blueprint XAS also allowed the optimisation of band-shape parameters to fit time-dependent DFT and Multiplet simulations to the experimental data.

In other more-recent computational developments, CoLoMoS, a semi-empirical tool written in terms of a strong-field representation basis set, aims to potentially become a very useful tool for XAS analysis in the evaluation of differential orbital covalency. While simulations on metal L-edge XAS have begun to be tested, the implementation of charge-transfer multiplets in ligand K-edge XAS is under development. Systems in which the assignment of specific features in the pre-edge is ambiguous could produce reconciled results through the use of this latter implementation. In addition to the Cl K-edge XAS data for compounds 2a and 2b that fall into this category, the Cl K-edge XAS data for compounds 3a (or 3b) serves as an additional good example of this.

Figure 7.1a shows the Cl K-edge XAS data for compound 3a. While the fitting of the data can provide information about covalency in terms of the individual components in the evaluation function (e.g., $f_{P1}-f_{P4}$), the differential orbital covalency might not be as
easily extracted, considering that ground-state DFT (Table 5.4 [Page 174] and Figure 5.17 [Page 177]) and time-dependent DFT + Slater ∆SCF computations (Figure 7.1b) suggest that these features are due to transitions to more than one kind of orbital (e.g., ruthenium-based versus carbene-based, etc). Therefore, to be able to extract differential orbital covalency from these systems, it can be envisaged a situation in which the output of CoLoMoS-based simulations can be used as a feed for one peak function of the evaluation function for fitting in Blueprint XAS. The design of an algorithm capable of such computation should allow not only the regular exploration of the fit parameters in Blueprint XAS but also the computation of the multiplet simulations from a reasonably large pool of charge-transfer parameters with well-chosen lower and upper bounds. The investigation of the effect and significance of having different off-diagonal T parameters in these simulations is also necessary to help define lower and upper limits for such parameters. Extending this to other systems, this approach can also be beneficial to evaluate hyperconjugation effects (214, 215).

Regarding the results on compounds 1-7 presented in this thesis work, strong evidence from the Ru K-edge XAS data has shown that the ruthenium centre is more positively charged in the second generation analogues along the series. Computational studies revealed that the origin of this may come from the combined effects of considerable π-back-bonding together with less σ-donation from the NHC ligand, in comparison with the larger σ-donation observed for PCy3. Ground-state DFT studies additionally revealed a similar overall bonding structure in each pair of analogues in the series 1-5, suggesting that the changes on the charge on the metal centre should be due to the substitution of the ancillary ligand. The Cl K-edge analysis results on compounds 1a and 1b are consistent with these results and suggest similar charge donations from the chlorine to the ruthenium centre in the Grubbs complexes (1a, 1b). In addition, a very similar distortion along the ruthenium-carbene sigma bond was observed for these two complexes. To a certain extent, this was also the case also for compounds 2a and 2b. However, two possible scenarios in the electronic structure of these two compounds were considered. In the first scenario, the LUMO is assumed to be the carbene-based MO. Under this umbrella, a large spitting between the transitions to the two Ru-4d (~1.2 eV) based MOs in the Cl K-edge is observed, possibly as a
consequence of the differences in relaxation effects between the two orbitals as the chlorine hole is being created. In the second scenario, the LUMO is assumed to be a Ru-4d based MO and the shoulder peak in the pre-edge of 2a and 2b is assigned to be the transition to the carbene-based orbital.

Figure 7.1  (a) Peak components around the Cl K-edge region in the evaluation function for the fitting of the Cl K-edge and Ru L_{2,3}-edges XAS data of compound 3a. (b) Time-dependent DFT with Slater ΔSCF energy corrections for the Cl K-edge of 3a.

The relative intensities of the two features in the pre-edge, assuming this last description correlates well with the DFT-calculated Cl-3p content in the Ru-4d based MOs, correlates poorly with Cl-3p contributions in the carbene-based MO and implies important errors in the DFT prediction of the relative energies of these orbitals.
The identity of the LUMO is an important piece of information needed to understand the reactivity of these family of complexes. According to the Frontier Molecular Orbital theory (FMO), if the LUMO in Piers complexes, as analogues of the active catalyst (A, Scheme 1.3), is indeed a ruthenium-based 4d-σ* MO, the interaction of the active catalyst A with the olefin may be occurring through sigma donation from the olefin to the empty ruthenium-based MO, as illustrated in Figure 7.2a. Under these circumstances, the catalyst would be formally behaving as an electrophilic Fischer-like carbene. However, if the LUMO is the carbene-based π_{Ru=C}* MO, the initial interaction between the active catalyst A and the olefin may be happening via interaction of the occupied carbene-based π_{Ru=C} bonding MO in the catalyst with the π_{C=C}* anti-bonding MO in the olefin, as illustrated in Figure 7.2b. This scenario would be in better agreement with the behaviour expected for a nucleophilic, Schrock-like carbene.

The analysis of the Cl K-edge extended to the rest of the compounds in the series should provide additional clues to solve this puzzle. The results from multiplet simulations should also reveal important information. Finally, taking advantage of the good resolution of the data in the region of soft x-rays, the analysis of the C K-edge XAS data shown in this thesis should also provide additional details on the electronic structure of these compounds.

Overall, the experimental techniques and the corresponding methodologies employed for the analysis presented in this thesis work have proven to be very effective in providing experimental evidence for the determination of the electronic structure and the overall understanding of ruthenium-carbene complexes. These methods and techniques can serve as the foundation for the comprehensive study of other related species relevant to olefin metathesis, or in general, to other systems in the field of homogeneous catalysis. This is essential at present times where our current understanding help rationalise only certain aspects of the reactivity of these systems, but do very little to predict the behaviour of other new catalysts in the currently explored or in complete new reactions. In this sense, as more known catalytic systems get fundamentally understood in the fields of chemistry and biology, catalysis should
become more predictable, consequently contributing in the development of bolder theories that more effectively predict reactivity in all areas of chemistry.

Figure 7.2  Identity of the LUMO in ruthenium-based catalysts and its implications in the reactivity of the active catalyst (A) with the olefin. (a) The LUMO is a ruthenium-based 4d-σ* molecular orbital. (b) The LUMO is the carbene-based π_{Ru=C} bonding molecular orbital.
REFERENCES