Structure and bonding of sulfur-containing molecules and complexes

Theoretical and experimental x-ray absorption, vibrational spectroscopic and crystallographic studies

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2007
Cover:
Illustrates the sulfur K-edge XANES spectrum calculated for sulfur dioxide and the molecular orbital corresponding to the first transition of antibonding π* character.

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To Robert and my family.
THE MORE ACCURATE THE CALCULATIONS BECOME, THE MORE THE CONCEPTS TEND TO VANISH INTO THIN AIR.

-- R.S. MULLIKEN, J.C.P. 43,S2(1965)
Abstract

Synchrotron-based spectroscopic techniques enable investigations of the many important biological and environmental functions of the ubiquitous element sulfur. In this thesis the methods for interpreting sulfur K-edge X-ray absorption near edge structure (XANES) spectra are developed and applied for analyses of functional sulfur groups. The influence of coordination, pH, hydrogen bonding, etc., on the sulfur 1s electronic excitations is evaluated by transition potential density functional theory. Analyses have been performed of reduced sulfur compounds in marine-archaeological wood from historical shipwrecks, including the *Vasa*, Stockholm, Sweden and the *Mary Rose*, Portsmouth, U.K.. The accumulation of sulfur as thiols in lignin-rich parts of the wood on the seabed is also a probable pathway in the natural sulfur cycle for how reduced sulfur enters fossil fuels via humic matter in anaerobic marine sediments. Sulfur K-edge XANES spectra for several biochemical model compounds and for coexisting isomeric sulfur species in cysteine and sulfite(IV) aqueous solutions have been analyzed with the aid of theoretical calculations. Cysteine derivatives are important for biochemical detoxification, and mercury(II) cysteine complexes in solution have been structurally characterized by means of Extended X-ray Absorption Fine Structure (EXAFS), Raman and $^{199}$Hg NMR spectroscopy. Lanthanoid(III) ions were found to coordinate eight dimethyl sulfoxide oxygen atoms in a distorted square antiprism in the solid state and in solution, by combining crystallography, EXAFS, XANES and vibrational spectroscopy. The mean M-O bond distances for the disordered crystal structures are in good agreement with those from the lattice-independent EXAFS studies. The different sulfur K-edge XANES spectra for the dimethyl sulfoxide ligands in the hexasolvated complexes of the trivalent group 13 metal ions, Tl(III), In(III), Ga(III) and Al(III), were interpreted by theoretical calculations.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>dmso</td>
<td>Dimethyl Sulfoxide (in chemical formulae)</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide, ((\text{CH}_3)_2\text{SO})</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham density functional method</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock approximation</td>
</tr>
<tr>
<td>IP</td>
<td>Ionization Potential</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>Mesylate</td>
<td>Methanesulfonate, (\text{CH}_3\text{SO}_3^-)</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near-Edge X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>SCF</td>
<td>Self Consistent Field</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SSRL</td>
<td>Stanford Synchrotron Radiation Laboratory</td>
</tr>
<tr>
<td>SXM</td>
<td>Scanning X-ray Spectromicroscopy</td>
</tr>
<tr>
<td>TP</td>
<td>Transition Potential</td>
</tr>
<tr>
<td>Triflate</td>
<td>Trifluoromethanesulfonate, (\text{CF}_3\text{SO}_3^-)</td>
</tr>
<tr>
<td>Trichlate</td>
<td>Trichloromethanesulfonate, (\text{CCl}_3\text{SO}_3^-)</td>
</tr>
<tr>
<td>XAFS</td>
<td>X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
List of publications

This thesis is based on the results presented in the following papers which will be referred to by their Roman numerals in the text (reproduced by permission from Inorganic Chemistry, Acta Crystallographica, Physica Scripta and Proceedings of the National Academy of Sciences, U. S. A.):

I. Analyses of sulfur and iron in marine-archaeological wood
M. Sandström, Y. Fors, F. Jalilehvand, E. Damian and U. Gelius

II. Sulfur K-edge X-ray Absorption Spectra for Dimethyl Sulfoxide in the Solvated Thallium(III), Indium(III), Gallium(III) and Aluminum(III) Ions
E. Damian, F. Jalilehvand, A. Abbasi, L.G.M. Pettersson and M. Sandström

III. Sulfur accumulation in the timbers of King Henry VIII's warship Mary Rose: a pathway in the sulfur cycle of conservation concern
M. Sandström, F. Jalilehvand, E. Damian, Y. Fors, U. Gelius, M. Jones and Murielle Salomé
Proc. Nat. Acad. Sci., USA (PNAS), 102, 2005, 14165–14170

IV. Mercury(II) Cysteine Complexes in Alkaline Aqueous Solution
F. Jalilehvand, B. O. Leung, M. Izadifard and E. Damian

V. Sodium trichloromethanesulfonate monohydrate
E. Damian, L. Eriksson and M. Sandström
Acta Cryst., C62, 2006, m419-420

VI. Sulfur X-ray absorption and vibrational spectroscopic study of sulfite, sulfur dioxide and sulfonate solutions, and of the substituted sulfonate ions $X_3CSO_3^-$ ($X = H, Cl, F$)
Submitted to Inorganic Chemistry
VII. Theoretical and experimental sulfur K-edge X-ray absorption spectroscopic (XANES) study of cysteine, cystine, methionine and methionine sulfoxide
E. Damian, F. Jalilehvand, B. Leung, L.G.M. Pettersson and M. Sandström
In manuscript

VIII. Crystallographic and Vibrational Spectroscopic Studies of Octakis(dimethyl sulfoxide)lanthanoid(III) Iodides
Submitted to Inorganic Chemistry

IX. X-Ray Absorption Fine Structure Spectroscopic Studies of Octakis(dimethyl sulfoxide)lanthanoid(III) Complexes in Solution and in the Solid Iodides
I. Persson, E. Damian Risberg, P. D’Angelo, S. Panfilis, M. Sandström and A. Abbasi
Submitted to Inorganic Chemistry

Additional paper that was not included in this thesis:
The sulphur threat to marine archaeological artefacts: acid and iron removal from the Vasa
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1 Introduction

Sulfur is a ubiquitous element that is abundant in nature both in inorganic and organo-sulfur compounds, but also found as the free element. Even though sulfur compounds are of great importance in many diverse systems, the biochemical functions are not fully understood, mainly because few analytical techniques are available to characterize the sulfur species. However, synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy at the sulfur K-edge is being developed into a powerful tool to investigate sulfur compounds in a variety of samples. This method is sensitive to the electronic and structural environment of the sulfur atom and can therefore distinguish between inorganic and organo-sulfur forms. The shape, intensity and position of the peaks in the sulfur K-edge XANES spectra which originate from sulfur 1s electron excitations depend on the oxidation state and the surrounding of the sulfur atom. Their energy varies along a 14 eV range from sulfides (-II) to sulfates (VI).

Useful insights have been obtained by analyzing biological, environmental and even marine-archaeological samples. Sulfur K-edge XANES has been applied to determine the chemical speciation of sulfur in samples of blood and in other samples of biological importance, in fossil fuels such as sulfur-containing coal and oil, in sediments, and plants. This modern spectroscopic technique was utilized on marine-archaeological samples from historical shipwrecks such as the Vasa and the Mary Rose, and could reveal unexpected sulfur accumulation causing conservation concerns. Through such studies, better understanding has been achieved of the role of sulfur in different natural systems and its involvement in chemical processes and transformations within the sulfur cycle in nature.

In such studies quantitative speciation of the different chemical functional groups of sulfur in a sample has mostly been obtained as linear combinations of normalized XANES spectra of appropriate reference model compounds. The experimental XANES spectrum was then deconvoluted by means of a least square fitting procedure implemented in the DATFIT program within the EXAFSPAK package. Typical sulfur functional groups often occurring in XANES spectra of natural samples are thiols (R-SH), disulfides (R-SS-R’), sulfoxides (R_SO), elemental sulfur (S₈), pyrite (FeS₂), sulfate (SO₄²⁻) and sulfonates (R-SO₃⁻). However, in order to obtain reliable results it is essential that the chemical state and environment of the characteristic sulfur functional groups in the reference compounds is similar to that in the analyzed sample. In all fittings of spectra from the wooden samples from the Vasa and the Mary Rose, the experimental peak centered on 2476.4 eV assigned to sulfoxide compounds, was difficult to reproduce by the standards dimethyl sulfoxide and methionine sulfoxide. This deviation was assumed to be caused by the different surrounding around the sulfoxide group in the
sample and the reference compounds and has initiated part of the theoretical studies included in this thesis.

Part of the thesis focuses on changes induced in the experimental features of the sulfur K-edge XANES spectra by the bonding and the chemical environment of the sulfur atom. The experimental spectrum of dimethyl sulfoxide changes significantly upon coordination to some metal ions and the effects have been investigated by theoretical calculations. The peak energy position and the intensity of the experimental spectral features can be affected by various factors such as the pH of the solution, coordination or even hydrogen bonding. Several octakis(dimethyl sulfoxide)lanthanoid(III) iodides ([M(OSMe$_2$)$_8$]I$_3$; M = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Lu and Y), were structurally characterized by means of single crystal x-ray diffraction and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, while their vibrational spectra were analyzed by normal coordinate methods to connect bonding and structure.

For cysteine (XANES model compound for thiols) and methionine (a thioether), two sulfur-containing amino acids present in all cells, the influence of intermolecular hydrogen bonding interactions on the transition energies and intensities was assessed by means of theoretical calculations, as well as for their biochemically important oxidation products, the disulfide cystine and methionine sulfoxide. Two cysteine molecules can be reversibly oxidized to cystine, which consists of two cysteine residues joined by a disulfide bond. From XANES analyses of the ratio of these two biologically relevant functional groups (thiol to disulfide) in blood, the redox status of the system can be determined. Furthermore, we have calculated the theoretical spectra for cysteine and sulfite species present in aqueous solutions at different pH values, assigned the electronic transitions and analyzed the species coexisting within certain pH intervals. Cysteine derivatives are also important for detoxification, and EXAFS spectroscopy together with Raman and $^{199}$Hg NMR methods have been employed to characterize several mercury(II) cysteine complexes formed in alkaline aqueous solutions.

The system SO$_2$/H$_2$O is important from an environmental point of view and in the global sulfur cycle, especially since the SO$_2$-emission into the atmosphere, a major contributor to acid rain, has increased steadily over the last decades. The speciation of SO$_2$(aq) and sulfite solutions has been studied experimentally, as well as the sulfonate (HSO$_3^-$) and some substituted sulfonate anions (CX$_3$SO$_3^-$; X=H, Cl, F), by means of sulfur K-edge XANES and vibrational spectroscopy, evaluating structure and bonding. Throughout these studies, theoretical sulfur K-edge XANES calculations have been a primary tool to assess how the coordination, pH, hydrogen bonding and different chemical interactions influence the spectral features. The theoretical XANES spectra at the sulfur K-edge have been computed by means of the Density Functional Theory – Transition Potential (DFT-TP) method, al-
lowing interpretation and assignment of the peaks observed experimentally. By evaluating XANES spectra with theoretical calculations, valuable information about the electronic and geometric structure localized around the excited sulfur atom has been achieved.

The continuous development of synchrotron sources has opened up many new possibilities to experimentally analyze and characterize natural samples. The recent progress in theoretical description of the experimental XANES features and new achievements in the DFT-TP computer programs have enabled detailed interpretation of the spectral features and electronic structure of the compounds. This is another significant step forward, considering that the XANES region of x-ray absorption spectroscopy has so far mostly been utilized for qualitative assignments regarding the absorbing atom, such as local coordination environment and the oxidation state.

1.1 The Hard Soft Acid Base Principle (HSAB)

Different explanations have been proposed of the nature of the chemical bond in complexes that are formed in solutions. A useful description is the concept of Lewis acid-base reactions when metal ions interact with surrounding molecules, which are referred to as ligands. The central metal ion acts as the Lewis acid or electron pair acceptor, while each ligand acting as a Lewis base, donates one electron pair to the empty orbitals of the metal ion.

By comparing stability constants of metal complexes, Ahrland et al. in 1958 \(^\text{25}\) could classify the metal cations into class (a) and (b), where class (a) forms the strongest complexes with light donor atoms and class (b) with heavier donor ligands. Later, Pearson introduced the Hard Soft Acid Base principle (HSAB) \(^\text{26}\) to predict the stability of complexes, extending the idea of his predecessor to both acceptors (metal ions) and donors (ligands). Pearson classified the Lewis acids and bases as hard or soft, according to the principle: “Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases”. Thus, the “hard” and “soft” terminology can be associated to the previously introduced class (a) and (b) species, while intermediate species are known as borderline. Hard acids and bases include species that have small size, high oxidation state, low polarizability and high electronegativity and through hard-hard interactions form mainly ionic bonds. On the other hand, soft species possess opposite characteristics and generate through soft-soft interactions covalent bonds (cf: Table 1). One advantage of the description introduced by Pearson is that it can be applied to both inorganic and organic reaction chemistry. Similarly, most solvents act as either Lewis acids or bases; polar solvents such as water, alcohols and amines are hard Lewis basis. The ambidentate solvent dimethyl sulfoxide is an exception and can behave as either a hard or soft ligand when the oxygen or sulfur atom, respectively, acts as the electron pair donor.
Table 1. Classification of Lewis acids and bases (in ambidentate ligands the underlined element represents the site of attachment; cf. Ref. 27)

<table>
<thead>
<tr>
<th>Acids:</th>
<th>Borderline</th>
<th>Soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺, Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Ga³⁺, In³⁺, Sc³⁺, Ln³⁺, Ln: La-Lu</td>
<td>Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Rh³⁺, Ir³⁺, Ru³⁺</td>
<td>Cu⁺, Ag⁺, Au⁺, Tl⁺, Hg⁺, Pd²⁺, Cd²⁺, Pt²⁺, Hg²⁺</td>
</tr>
<tr>
<td>Bases:</td>
<td>NO₂⁻, SO₄²⁻, Br⁻</td>
<td>N₃⁻, N₂, C₆H₅NH₂</td>
</tr>
</tbody>
</table>

1.2 Solvents

1.2.1 Water (H₂O)

Water, the most abundant substance on the surface of Earth, is essential for life. It is a very efficient solvent capable of dissolving many compounds and electrolytes due to its high dipole moment (μ) and dielectric constant (ε). The water molecule, with two hydrogen atoms covalently bonded to an oxygen atom, belongs to the C₂ᵥ point group. The intermolecular hydrogen bonding interactions (O-H…O) between the water molecules are responsible for the many unusual physical properties of liquid water (cf. Table 2). Every water molecule can form at most four hydrogen bonds, accepting two through the lone pair of the oxygen atom and donating two through the hydrogen atoms in a tetrahedral arrangement. Such a tetrahedral surrounding is found in hexagonal ice (natural snow or ice) where the interatomic angles between nearby hydrogen bonded oxygen atoms are exactly 109.47°. In liquid water, however, the O-H…O bond distances and angles vary locally and are often broken. Recently, the molecular arrangement in the first coordination shell of liquid water has been investigated by combining theoretical and experimental studies of the oxygen K-edge x-ray absorption fine structure. The authors concluded that “most molecules in liquid water are in two hydrogen-bonded configurations with one strong donor and one strong acceptor hydrogen bond”.²⁸

1.2.2 Dimethyl sulfoxide (CH₃)₂SO

Dimethyl sulfoxide (DMSO) is a colorless liquid of low toxicity, which has for many years been used as an industrial solvent. DMSO has been alleged to have therapeutic value for treating arthritis and conditions affecting mus-
cles and bones. However, studies on animals indicated nasty side effects such as eye damage, headaches, nausea and skin rash. Whether or not DMSO is effective for drug purposes still seems uncertain. A special danger is that DMSO can easily penetrate the skin and is able to carry a wide spectrum of dissolved impurities through cell walls, which can have severe consequences for humans.

Dimethyl sulfoxide is an aprotic, highly polar solvent and can as ligand coordinate through either the oxygen or sulfur atom. Hard metal ions (cf. Table 1) such as Al\(^{3+}\), Ga\(^{3+}\), In\(^{3+}\), as well as the lanthanoid(III) ions form M-O bonds with ionic character via the oxygen atom, while e.g. Pd\(^{2+}\), Pt\(^{2+}\), Rh\(^{3+}\) and Ir\(^{3+}\) sometimes can bind via the soft sulfur atom. Some physical properties for dimethyl sulfoxide are given in Table 2.

**Table 2.** Some physical properties of water and dimethyl sulfoxide (DMSO).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>μ (D)</th>
<th>ε</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.0</td>
<td>100.0</td>
<td>1.85</td>
<td>78.5</td>
<td><img src="image" alt="WaterMolecule" /></td>
</tr>
<tr>
<td>DMSO</td>
<td>18.5</td>
<td>189.0</td>
<td>3.96</td>
<td>46.4</td>
<td><img src="image" alt="DMSOMolecule" /></td>
</tr>
</tbody>
</table>
2 Experimental section

2.1 Methods

2.1.1 X-ray absorption spectroscopy (XAS)

When the x-ray energy is close to the absorption edge of an element in an irradiated sample, a core electron can be excited creating a core hole in an inner electron shell of an atom. The electronic transition occurs into empty valence or Rydberg levels for energies below the ionization threshold (excitation, cf. Fig 1a) or creates a photoelectron above the threshold (ionization, cf. Fig. 1b). This leads to a highly excited state, which decays within a few $10^{-15}$ s by filling the hole with a valence electron. The excess energy is released via different mechanisms, either through a radiative process by emitting a photon (fluorescence, cf. Fig. 1c) or via a non-radiative process by ejecting Auger electrons (cf. Fig. 1d). The Auger process dominates for light elements with a rather low fluorescence yield at the K-edge (~0.1% for sulfur), which increases with increasing atomic number Z.

![Figure 1](image.png)

**Figure 1.** When an atom absorbs a photon creating a core hole, the core electron can be (a) excited into unoccupied valence states, or (b) ejected as a photoelectron. The excess energy is released through two main decay channels, emitting (c) a photon in fluorescence or (d) Auger electrons.

Since the binding energy of the electrons has a specific value for each shell within an atom, which also is different for each element in the periodic table, XAS is a local, atom-specific probe of the unoccupied electronic states. Rehr et al. have proposed that the resulting x-ray absorption spectrum conveniently can be divided into two different regions (cf. Figure 2):

1) The unified multiple scattering (MS) XAFS (X-ray Absorption Fine Structure) region extending from about –10 to 50 eV around the edge;

2) The Extended X-ray Absorption Fine Structure (EXAFS) region that covers the photon energy range from 50 to about 1000 eV above the absorption edge.
The unified MS XAFS region includes both the XANES (X-ray Absorption Near Edge Structure) and NEXAFS (Near Edge X-ray Absorption Fine Structure) regions. The former covers the ± 10 eV interval around the edge, while the latter extends from about a few eV to 50 eV above the edge.\textsuperscript{30b}

Figure 2. The main regions, multiple scattering XAFS and EXAFS, of the Sm L\textsubscript{III}-edge absorption spectrum of the solid compound Sm(dmso)\textsubscript{8}I\textsubscript{3}, recorded in transmission mode (see Data collection, Section 2.2). The multiple scattering (MS) and single scattering (SS) processes, which dominate the unified MS XAFS and EXAFS regions, respectively, are schematically illustrated.

**XANES:** For sulfur, intense K-edge spectral absorption features in the XANES region correspond to transitions of the 1s electron into unoccupied molecular orbitals (MOs) below the ionization potential (IP) such as valence or Rydberg states. The electronic transitions obey the dipole selection rules, which state that only transitions between orbitals whose orbital angular momentum quantum number \(l\) differ by one unit are allowed (\(\Delta l = \pm 1\)) and that the total spin \(s\) must be conserved (\(\Delta s = 0\)) during excitation. Therefore, according to the \(\Delta l = \pm 1\) rule, for the K-edges only transitions into MOs having local p-character are allowed.

Compounds especially of transition metals and covalently bonded elements absorbing at low energy display pre-edge features whose shape, height and absolute position, depend on the geometrical arrangement around the absorber atom and its oxidation state, thus providing structural information about the absorber atom. However, detailed theoretical interpretation of the XANES data has proved to be quite complex, unlike for the EXAFS oscillations, see below.\textsuperscript{31,32}

An empirical method, especially developed for sulfur-containing samples, is normally employed when an XANES spectrum is used to identify and quantify the species present in a sample (see Chapter 4). In short, a linear combination of normalized spectra of appropriate standard compounds is
then fitted to the experimental spectrum by means of a least-square procedure.

**NEXAFS**: The broader peaks observed in the NEXAFS region correspond to transitions into continuum states above the IP value, which generates photoelectrons with relatively low kinetic energy. The multiple scattering contributions to this NEXAFS region are significant; they appear due to the scattering of the photoelectron by the atoms present in the first shell around the absorber atom. New developments have improved the description of the multiple scattering processes involved in the NEXAFS part of the spectrum.\(^{29,31}\)

**EXAFS**: Single backscattering (SS) processes from atoms nearby the absorber atom dominate in the EXAFS region. The sinusoidal oscillations observed in the EXAFS region are a consequence of the constructive and destructive interference between the outgoing and backscattered photoelectron wave, as illustrated in Fig. 3. However, multiple scattering (MS) processes, where the photoelectron wave scatters from more than one neighbor atom, can make a significant contribution also in the EXAFS region. The aim of the EXAFS data analysis is to obtain structural properties such as interatomic bond distances between the absorber and its neighbors, as well as the number and type of backscattering atoms in the coordination shells. The EXAFS oscillations, \(\chi_j\), can be modeled by means of the expression:

\[
\chi_j(k) = \sum_{j} \frac{N_j S_0^2(k)}{kR_j^2} \left| f_{\text{eff}}(k) \right|_j e^{-2k^2\sigma_j^2} \frac{-2R_j}{\Lambda(k)} \sin[2kR_j + \phi_{ij}(k)]
\]

where the parameters are: the number \(N_j\) of backscattering atoms at the mean distance \(R_i\) from the absorber in the \(i\)th shell; the Debye-Waller parameter \(\sigma_j^2\) related to the mean-square variation in a Gaussian distribution of distances around \(R_j\); the scattering variable \(k\); the effective amplitude function \(\left| f_{\text{eff}}(k) \right|_j\); the total phase-shift \(\phi_{ij}(k)\) of the absorber-scatterer pair; the photoelectron mean free path \(\Lambda(k)\), and the amplitude reduction factor \(S_0^2\).

For an assumed model, the phase shift, mean free path and amplitude functions for the single and multiple scattering pathways, are nowadays calculated by *ab initio* methods by means of e.g. the FEFF program.\(^{33}\) The \(N_j\), \(R_i\), \(S_0^2\) and \(\sigma_j^2\) parameters are refined through a least square fitting trying to minimize the differences between the experimental and theoretical EXAFS oscillations.
Figure 3. The EXAFS modulations (cf. Figure 2) are created by interference between the outgoing and backscattered photoelectron waves giving rise to oscillations due to destructive (a) and constructive (b) interference.

2.1.2 X-ray Photoelectron Spectroscopy (XPS)

XPS or ESCA\(^{34}\) (Electron Spectroscopy for Chemical Analysis) represents an application of the photoelectric effect. This phenomenon occurs when an incident photon transfers its energy to the emitted photoelectron, as illustrated in Fig. 1b. The atom is ionized when the incoming photon of well-defined energy \(E_{\text{photon}}\) ejects one of the core electrons creating a core hole. By measuring the kinetic energy of the photoelectron \(E_{\text{kinetic}}\) the electron binding energy of the core electron \(E_{\text{binding}}\) can be obtained:

\[
E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}}
\]  

(2)

With this method all elements (except hydrogen) in a sample can be identified and quantified because the intensity of a peak is proportional to the atomic concentration of that element. However, XPS is a very surface sensitive method of analysis because the ejected photoelectrons might be captured by the surrounding matter and not reach the detector. The maximum escape depth is about 100 Å. Different chemical environments of the absorbing atom lead to so-called chemical shifts in XPS, which correspond to differences in the core electron binding energies providing information about the local surrounding. Moreover, additional features are observed in the spectra that are caused by secondary processes such as Auger decay (Fig. 1d), shake-up and shake-off transitions, but this will not be discussed further in the present context.

In Figure 4, two distinct sulfur 2p core level lines are observed, \(S_{\text{red}}\) and \(SO_4^{2-}\), which correspond to reduced and oxidized sulfur, respectively. The chemical shifts often provide useful information about the oxidation state of an element of interest in the sample since the higher the oxidation state the higher the binding energy.
Figure 4. XPS spectra of a *Vasa* oak wood core sample (core 13) at different depths. The energy region 145-210 eV shows the presence of the following elements: chlorine, boron, sulfur and silicon. The amount of oxidized sulfur decreases with increasing depth while the amount of reduced sulfur and boron is almost constant throughout the core. The peaks denoted SO$_4^{2-}$ and S$_{red}$ illustrate the S(2p) chemical shift explained above. The high amount of silicon at the surface probably originates from silicate particles. Some silicate is also found at 20 mm depth, together with some chlorine and sulfate, indicating a crack in the wood.

From the XPS spectrum of an oak core sample (core 1b) from the *Mary Rose*, three different types of sulfur species (oxidized 1, reduced 3, and the intermediate sulfoxide (R$_2$SO) 2) could be refined through a least square curve fitting procedure. For each type of sulfur species considered in the fitting, two symmetrical Gaussian shape components were required that correspond to excitation of sulfur 2p electrons from the 2p$_{1/2}$ and 2p$_{3/2}$ states, respectively (*cf.* Figure 5). During the fitting, the position and the height of the peaks and the full width at half maximum (FWHM) of one of the components were varied, keeping the spin-orbit splitting to 1.18 eV between the sulfur 2p$_{1/2}$ and 2p$_{3/2}$ states for each species. Several constraints were applied, i.e. all components were restricted to the same FWHM, and the intensity ratio between the S2p$_{1/2}$ and S2p$_{3/2}$ components for each species was fixed to 1 : 2.
**Figure 5.** Curve fitting of XPS spectra of oak core 1b (92.5 mm depth) from a magazine stored oak beam from the *Mary Rose* hull, with three types of sulfur species, 1: oxidized (mostly sulfate SO$_4^{2-}$), 2: sulfoxide (R$_2$SO) and 3: reduced sulfur. The mean S 2p$_{3/2}$ binding energies (after calibration) for the three components 1, 2 and 3 were 168.8, 166.3, and 163.7 eV, respectively.

### 2.1.3 Vibrational spectroscopy

Vibrational spectroscopy probes the molecular vibrations within the sample. It is widely used for qualitative chemical analysis, e.g. for pharmaceutical, food and agrochemical quality control in industry. However, detailed analysis of the vibrational frequencies measured by infrared absorption (IR) and Raman spectroscopy techniques also provides in depth information about the molecular structure and chemical bonding. Even though both the experimental techniques (IR and Raman) for obtaining vibrational spectra measure the vibrational frequencies they are complementary with different selection rules; i.e. transitions allowed or strong in IR are often forbidden or weak in Raman and the opposite. For example, for highly symmetric polyatomic molecules with a center of inversion the Raman active vibrations are not IR active and vice versa, because of the mutual exclusion rule.$^{35,36}$

#### 2.1.3.1 Infrared (IR) absorption

In the IR absorption process, photons of certain energies are absorbed by the sample when exposed to incident radiation of varying wavelength *(cf. Figure 6)*. The energy of the absorbed photons matches the separation between two vibrational levels within the molecule in the ground state. However, such transitions only occur if the dipole moment of the molecule changes during the vibration. Totally symmetric vibrations do not change the dipole moment and will therefore be IR-inactive.
The IR spectrum is for practical reasons divided into three main spectral regions: far-IR (200-10 cm\(^{-1}\)), mid-IR (4000-200 cm\(^{-1}\)) and near-IR (12820-4000 cm\(^{-1}\)).\(^{35}\) The far-IR region provides information about metal-metal bonds and metal-ligand interactions, while the mid-IR region contains bands specific to common functional groups of the molecule (group functional region: 4000-1300 cm\(^{-1}\)) as well as the fingerprint region (1300-900 cm\(^{-1}\)) of fundamental skeletal modes, which provides a unique pattern for each organic compound. The near-IR probes overtones and combination bands and is used for qualitative analytical purposes in the food and pharmaceutical industries as well as in medicine to provide medical diagnostics.

![Vibrational transitions within a molecule absorb IR radiation of specific energy, hv\(_{\text{vib}}\).](image)

**Figure 6.** Vibrational transitions within a molecule absorb IR radiation of specific energy, hv\(_{\text{vib}}\).

### 2.1.3.2 Raman scattering

Raman spectroscopy is connected to the scattering of light by the sample. When irradiating the sample by monochromatic light, most of the radiation will be scattered elastically (i.e. without energy loss or Rayleigh scattering) and a very small amount inelastically (i.e. with energy loss and known as Raman scattering). The Raman scattering is produced due to interactions between the incident photons and the vibrational energy levels of the molecule. A molecular vibration is Raman active if the polarizability of the molecule changes during the vibration. If the molecule gains vibrational energy, the scattered radiation with lower energy than the incident radiation, hv\(_{0}\)-hv\(_{\text{vib}}\), is referred to as Stokes lines, while for the anti-Stokes lines the incident radiation gains energy, hv\(_{0}\)+hv\(_{\text{vib}}\), cf. Figure 7. Therefore, the energy (often measured as wavenumbers, cm\(^{-1}\)) of the Stokes and anti-Stokes lines provides information about the vibrational energies of the molecule. At ambient temperature most molecular vibrations are in the ground state, making the Stokes lines more intense than the anti-Stokes.
2.1.4 Force constant and bond strength

Vibrational transition energies are sensitive to small variations in the molecular bonding conditions, making vibrational analysis a useful tool for comparisons of bond strength, distances and angles in related compounds, both in solution and the solid state. Thus, by analyzing the vibrational spectra valuable information about the coordination geometry and the new metal-ligand bonds formed in metal complexes can be achieved.

Force constants characteristic for bond stretching and angular deformation, can be obtained by normal coordinate analysis. For several series of diatomic molecules the force constant and dissociation energy $D_e$ of the bond decrease simultaneously. This suggests that the force constant could be proportional to the bond strength. Yet, such a relationship is only valid for a series of related compounds, because the force constant is a measure of the curvature of the potential energy close to the equilibrium bond distance, while the dissociation energy is defined as the depth of the potential energy curve (cf. Fig. 8). A steep potential energy function is consistent with a large force constant. Some empirical formulas have been deduced correlating the force constant to the bond distance, as described elsewhere.

For diatomic molecules, the vibrational frequency of a bond in the harmonic oscillator approximation is connected to the force constant through the formula:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

(3)

where $\nu$, $\mu$ and $K$ represent the frequency, reduced mass of the system and the force constant, respectively. In reality, the molecular vibrations are...
slightly anharmonic, which allows for otherwise forbidden weak overtones and combination bands in the vibrational spectra. Nonlinear polyatomic molecules (N atoms) have 3N-6 fundamental modes (3N-5 for linear molecules) in their vibrational spectra. The observed frequencies depend on both kinetic and potential energy of the normal modes, for all types of interactions between the atoms.

Normal coordinate analysis (NCA) was employed to assign and calculate all the observed vibrational frequencies by evaluating the force constants that describe the interatomic forces within some molecular species and complexes. Such evaluation of the experimental vibrational frequencies and the force field has been undertaken for several metal-DMSO complexes as well as for a number of related oxosulfur species. Important information about changes in bond strength and coordination has been achieved for the investigated systems.

![Figure 8](image)

**Figure 8.** The shape of the potential energy curve for a diatomic molecule in *left* harmonic approximation and with *right* anharmonic potential function, with vibrational energy levels and dissociation energy indicated. Figure adapted after Ref.35, chapter 1, page 30.

### 2.1.5 Normal Coordinate Analysis

The calculation of the experimental vibrational frequencies and the force constants for the studied systems was carried out by means of Wilson’s GF matrix method using a PC-based program package developed by J. and L. Mink. Detailed descriptions of the principles can be found elsewhere. As mentioned above, the kinetic and potential energies of the system determine the experimental frequencies. The kinetic energy, \( T \), depends on the geometrical arrangement of the atoms and their masses \( m_{ij} \), while the potential energy, \( V \), due to the interactions within the molecule is usually defined in terms of the force constants \( F_{ij} \). Their expressions in terms of internal coordinates \( S \) (bond stretching and angle deformation) are given below:
\[
T = \frac{1}{2} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} (G^{-1})_{ij} \dot{S}_i \dot{S}_j
\]  

(4)

\[
V = \frac{1}{2} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} F_{ij} S_i S_j
\]  

(5)

where \( G^{-1} \) stands for the inverse of the \( G \) matrix which is describing the kinetic energies in terms of mass-weighted Cartesian displacements and \( S = \frac{dS}{dt} \).

The theoretical frequencies can be obtained by solving the secular equation:

\[
| \mathbf{G}\mathbf{F} - \mathbf{E} \lambda | = 0
\]

(6)

where \( \mathbf{E} \) is the unit matrix, \( \mathbf{F} \) is a matrix representation of the potential energies and \( \lambda \) is the eigenvalue related to the frequency \( \nu \) through the relation:

\[
\nu = \frac{1}{2\pi} \sqrt{\lambda}
\]

(7)

Hence, the frequencies can be calculated from (7) if the force constants and the masses of the atoms are known.

Generally, the frequencies are determined experimentally whereas the force constants are unknown. In such cases the solutions need to be obtained through an iterative procedure. An initial set of force constants is introduced to calculate the theoretical frequencies followed by least-square refinement of the force constants, minimizing the difference between the observed and calculated frequencies. The initial force constants are usually obtained from molecules with similar bonds. For large systems some approximations are necessary because the number of experimental frequencies is always smaller than the number of unknown force constants. An important way to increase the number of experimental frequencies is the use of isotopic substitution, because the force constants do not depend on an isotopic increase of the mass of an atom. The number of refined force constants can be reduced by neglecting some less important interactions (e.g. interactions between non-bonded atoms), and by correlating or fixing some parameters. Despite the approximations, refined force constants provide valuable information on the nature of the interatomic forces, especially when comparing consistent sets for related molecular species.
2.2 Data collection

2.2.1.1 XANES measurements

The sulfur K-edge XANES measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) at the wiggler beamline 6-2, taking advantage of the synchrotron radiation properties, such as high intensity and tunability over a wide energy range. The x-ray radiation was monochromatized by means of a double silicon crystal monochromator Si(111) and higher order harmonics rejected by means of a Rh-coated silicon mirror. The fluorescence signal $I_f$ emitted from a sample was detected by Lytle detector with a nitrogen gas-filled ion chamber, while monitoring the intensity, $I_0$, of the incident beam using a helium-filled gas ionization chamber. For measurements at the sulfur K-edge corresponding to the 2.5 – 3 keV energy range, the beam path and sample chamber were kept in helium of atmospheric pressure to avoid vacuum at the sample. The energy scale was calibrated by setting the lowest energy peak of sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3\cdot5\text{H}_2\text{O}$) to 2469.2 eV.\(^{38}\)

2.2.1.2 Experimental setup

In X-ray absorption spectroscopy structural information is obtained from the fine structure of the absorption coefficient $\mu(E)$ at energies at or above the absorption edge of an atom. Samples in any physical state can be studied. Depending on sample concentration, thickness, homogeneity, etc. the spectrum can be measured in two principally different ways, see Figures 9 and 10:

a) transmission mode; the absorption is measured directly by recording the transmitted intensity $I$ through the sample of thickness $x$ when irradiated by the incident beam of intensity $I_0$ as a function of the energy $E$, according to the expression: $I_1 = I_0 \cdot e^{-\mu x}$. This detection mode is preferred for rather concentrated samples. The calibration of the energy scale is preferably performed simultaneously, by collecting the absorption spectrum of the pure element (foil) or another well-defined compound of the absorbing element with known absorption energy. The foil is usually placed between the second and third ion chambers.

![Diagram](image)

**Figure 9.** The setup used for XAFS experiments in transmission mode.
b) fluorescence mode; the fluorescence x-rays emitted when the created core hole is refilled by electrons occupying the outer shells are collected. In this case, the intensity of the emitted x-rays $I_f$, is proportional to the number of core holes created, even though for low atomic numbers $Z$ the fluorescence yield can be low. The absorption coefficient can be expressed as $\mu(E) \approx I_f/I_0$ and fluorescence spectra can be recorded for dilute samples, then often by means of a very sensitive Ge-detector. The Lytle detector handles higher count rates and can be used also for concentrated samples.

![Diagram of XAFS setup](image)

**Figure 10.** The setup used for XAFS experiments performed in fluorescence mode.

### 2.2.2 XPS measurements

An XPS spectrum records the kinetic energy of the emitted photoelectrons. Al K$_\alpha$ x-ray radiation (1486.6 eV) obtained from a rotating Al-anode is monochromated by several toroidally bent quartz crystals and passes through a thin Al foil before being focused on the sample. The kinetic energy of the photoelectrons is determined by means of a hemispherical electron energy analyser. The outgoing photoelectrons are collected by a multi-element lens, which uses high voltage to accelerate/retard the electrons to suitable analyzing energy and focuses them on a slit aperture pair at the entrance plane of the hemispherical electron energy analyser. The analyser contains an inner and an outer sphere, with an electric potential difference that allows the photoelectrons with a given kinetic energy to pass through. In our case, the “pass energy” was set to 300 and 500 eV, respectively. The resolution of the instrument becomes higher for lower pass energy. The photoelectrons are dispersed by the electrostatic field between the two hemispherical surfaces depending on their kinetic energy and electrons with different energies will arrive on different spots on the detector. The multichannel detector is mounted at the exit of the hemispherical analyser and consists of an assembly of microchannel plates, a phosphorescent screen and a CCD camera. The photoelectrons reaching the detector generate spots on the phosphorescent screen that are registered by a CCD ((Charge-Coupled Device) camera. The
latter is connected to the data acquisition system. A schematic view of the setup is given in Figure 11.

![Figure 11. The setup of the Scienta ESCA-300 instrument utilized to record the XPS spectra.](image)

The wood cores were cut at different depths into thin slices of maximum 1.5 mm and placed in the ultrahigh vacuum chamber (UHV) of the Scienta ESCA-300 instrument. The vapour pressure from the samples was pumped down below $1 \times 10^{-7}$ Pa. Such samples are insulators and when the photoelectrons are removed from the sample its surface will become positively charged. The charging may not be uniformly distributed across the material. A consequence of a non-uniformly charged surface is that the peaks will be broader and shifted to higher binding energies than in the case of a conducting sample. In order to prevent such effects, the surface potential is stabilized by bombarding the sample with low energy electrons from the flood gun (filament) incorporated inside the sample chamber. Due to the charging effect a calibration of the energy scale is required, usually using the C 1s binding energy of hydrocarbon as a reference peak. The hydrocarbons can be present in the sample itself or might be some contamination of the sample surface, e.g. by oil from the vacuum pumps.

A different reference peak was used for the *Vasa* samples, because a mixture of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and boric acid, $\text{B(OH)}_3$, dissolved in polyethylene glycol (PEG) was utilized as fungicide during the spraying with conservation liquid of the hull of the historical warship *Vasa*. The boron has penetrated throughout the wood, as observed in the XPS spectra of the *Vasa* core in Figure 4. Thus, the *Vasa* samples were calibrated against the B 1s peak which was set to 192.4 eV, while for the other samples, the C 1s peak was used as the reference peak, which was set to 285.0 eV.
2.2.3 IR and Raman measurements

All IR and Raman measurements were performed at ambient temperature. Raman spectra of solid compounds have been collected by means of a Renishaw System 1000 spectrometer, equipped with a Leica DMLM microscope, a 25 mW diode laser (782 nm) and a Peltier-cooled CCD detector. The Raman spectra of sulfite aqueous solutions at different pH (paper VI) were measured by means of a dedicated BioRad FT-Raman system equipped with a Spectra Physics Nd-YAG laser (1024 nm, 200 mW). The mid-IR absorption spectra (range 400–4000 cm\(^{-1}\), resolution 4 cm\(^{-1}\)) for the compounds discussed in paper VI were recorded using a purged Bio-RAD Digilab FTS 6000 FT-IR spectrometer, while for the samples discussed in paper VIII a Bio-Rad (Digilab) FTS 175 spectrometer was used. Finally, the far-IR spectra (50 – 700 cm\(^{-1}\), 2 cm\(^{-1}\)) for the DMSO solvates were obtained from a Bio-Rad (Digilab) FTS-40 spectrometer (paper VIII).
3 Theoretical background

3.1 Density Functional Theory (DFT) approach vs. Hartree-Fock (HF) method

The development of synchrotron sources that provide x-rays with a number of unique properties: high brightness, highly collimated and polarized, emitted in very short pulses in a wide range of energies, and which can easily be monochromatized to the required energy, have improved the resolution and therefore the richness of features in the molecular spectra. The experimental achievements have promoted the development of new computer software to calculate properties and also to interpret the observed electronic transition features theoretically.

To compute the properties of a system, a first step is to find its wave function ($\psi$), obtained by solving the time-independent non-relativistic Schrödinger equation written generally as:

$$\hat{H}\psi = E\psi \quad (8)$$

where $\hat{H}$ is the Hamiltonian operator of the system (which can be written as the kinetic ($T$) and potential ($V$) energies of the nuclei and electrons), $E$ is the total energy of the system, $\psi$ is the wave function that describes the system of interest. The Schrödinger equation can be solved exactly only for one-electron systems without electron–electron interactions, such as the hydrogen atom. As the number of electrons in a system increases, the electron correlation contribution arising from electrons interacting with one another becomes more important and the complexity of the Schrödinger equation increases and certain approximations are necessary.\(^{40}\)

The Hartree–Fock (HF) method,\(^{41,42}\) which was for many years employed to obtain approximate solutions for the electronic Schrödinger equation, gave satisfactory results for many properties. Hartree–Fock theory takes advantage of the variational principle, which states that any approximate wave function has an energy that is always greater than the energy for the exact wave function. The molecular orbitals are expressed as a linear combination of pre-defined basis functions $\chi$ as follows:

$$\varphi_i = \sum_{\mu=1}^{N} c_{i\mu} \cdot \chi_{\mu} \quad (9)$$

where $c_{i\mu}$ represent the molecular orbital expansion coefficients. The solution to the HF equations is accomplished when one has found the set of coefficients that minimize the energy of the resultant wave function. This is achieved by an iterative procedure leading to a self-consistent solution, i.e., the self-consistent field (SCF). In the HF molecular orbital theory the wave function $\psi$ is written as a determinant of molecular orbitals $\varphi_1, \varphi_2, \ldots, \varphi_n$. 
which fulfills the requirement of an antisymmetric wave function. In the SCF procedure, an initial set of coefficients are guessed for the molecular orbitals to generate a new set of coefficients. The procedure is repeated until the convergence criteria are met. However, in this approach, the electron correlation is neglected or the electron – electron repulsion is only included as an average effect. An improved description of such systems where the contribution from instantaneous electron – electron interactions is essential for accurate prediction of properties is obtained by so-called post-SCF or electron correlation methods, e.g. Configuration Interaction (CI), Many-body Perturbation Theory (MBPT) and Coupled Cluster (CC).

Since the energy calculated by the HF method accounts for ~99% of the total energy of the system, the electron correlation methods use the HF wave function as a starting point when near-degeneracy effects can be neglected; adding correlation corrections to the basic HF model. The HF wave function is augmented with additional functions to account for the instantaneous electron – electron interactions, improving the description of the valence orbitals since the valence electrons are involved in the chemical bonding where the chemical changes are taking place. These methods provide more accurate results, in better agreement with the experiment than the HF method, but the price of accuracy is paid in terms of computational time, which increases as a power of the number of electrons and the number of orbitals and these methods are therefore applicable only to relatively small systems.

The breakthrough to this problem came, beside the continuing advances in computer hardware and more efficient algorithms, with the development of the Density Functional Theory (DFT). Its implementation into computer codes has revolutionized the field of computations. By means of DFT one can acquire greater accuracy than with the HF method at approximately the same computational cost as a result of computing the electron correlation via general functionals\(^\dagger\) of the electron density. The accomplishments acquired by DFT calculations are a consequence of the research work started among others by Dirac, and continued by Hohenberg, Kohn and Sham, who are the founders of modern DFT. The first Hohenberg – Kohn theorem\(^\ddagger\) states that the external potential and therefore the total energy is a unique functional of the electron density \(\rho(r)\), i.e., one cannot have two different densities for the ground state. The consequence of expressing the energy in terms of the density is that if the system size increases, the dimensionality of the electron density \(\rho(r)\) is not affected since it only depends on the three space coordinates, while the wave function is directly proportional to the number of electrons. However, that theorem does not provide the functional expression that connects the electron density with the energy. Their second theorem shows

\(^\dagger\) A functional is defined in mathematics as a function of a function. In this case, the energy is a function of the electron density that is itself a function of the coordinates in real space.
that the ground state energy can be calculated by means of the variational principle by determining the electron density that minimizes the total energy of the system. In the Kohn – Sham formalism, the kinetic energy functional is divided into two different terms, one that can be calculated exactly assuming a hypothetical system with non-interacting electrons, which provides about 99% of the total kinetic energy, and the other as a small correction term. This reformulation improves the kinetic energy value achieved with the kinetic energy functionals introduced previously. Taking all that into account, the energy can be expressed in several components, which are computed separately as functionals of the electron density:

\[ E(\rho) = T(\rho) + E_V(\rho) + E_J(\rho) + E_{XC}(\rho) \]  

(10)

where \( T(\rho) \) is the kinetic energy of the hypothetical system, \( E_V(\rho) \) is the potential energy due to the electron – nuclei attraction and the repulsion between pairs of nuclei, \( E_J(\rho) \) is the potential energy due to the electron – electron repulsion, and finally \( E_{XC}(\rho) \) is the exchange-correlation energy accounting for the remainder of the electron-electron interactions. The last term, \( E_{XC}(\rho) \), is usually divided into two components, the exchange functional, \( E_X \), and the correlation functional, \( E_C \), corresponding to exchange and dynamical correlation, respectively. However, the \( E_{XC} \) value is dominated by the exchange energy contribution. These two functionals can be of two different types:

- **local** functionals which depend only on the electron density \( \rho \). This approximation is based on the assumption that the density locally can be treated as a uniform electron gas.
- **non-local** or gradient-corrected functionals that involve both the electron density \( \rho \) and their derivatives (gradients), \( \nabla \rho \). This approach assumes the local density to be a non-uniform gas.

Various expressions for the exchange and correlation functional have been proposed for the \( E_{XC} \) energy, which if the exact functional were known, would allow us to obtain the exact total energy of the system. Throughout our investigations we have employed non-local functionals namely the exchange functional of Perdew and Wang, and the correlation functional of Perdew.  

### 3.2 StoBe-deMon DFT calculations of XANES spectra

The theoretical calculations are now playing an increasingly important role in the interpretation and assignment of the features observed in the experimental spectra. XANES spectroscopy provides a tool for probing the electronic structure in close vicinity of the excited sulfur atom. By comparing the experimental and simulated XANES spectra one can achieve better under-
standing of the electronic structure and character of the chemical bonding of the investigated compounds.

To obtain the entire theoretical spectrum for a system would in general require computing state-by-state the excitation energies and oscillator strengths (or intensities) for all transitions allowed. The excitation energies would then be calculated as differences in total energies between the initial (ground state) and final states (excited states, for K-edge with a 1s core hole and an electron in different previously unoccupied orbitals). The corresponding intensities would then be obtained by computing the non-orthogonal transition moment between the initial and final states. However, this approach is quite complicated, time-consuming and limited to rather few states.

The transition potential method (TP), which is based on the transition state assumption by Slater,\textsuperscript{46} provides a much simpler computational approach. In the approximation introduced by Triguero \textit{et al.}\textsuperscript{24} half an electron is removed, leaving therefore only ½ electron in the 1s orbital of the excited sulfur atom in our case. This allows the full XANES spectrum to be obtained in a single computation, since the initial and final states are obtained from the same wave function described by the half occupied core hole. Furthermore, it accounts for relaxation effects of the final state up to second order\textsuperscript{46} and reproduces the transition energies to within 2 eV of the experimental values on an absolute energy scale. The additional \(\Delta\text{Kohn-Sham}\) corrections, where the fully relaxed excitation to the LUMO is calculated in addition to relativistic effects (+7.4 eV) on the S 1s ionization potential, provide a final absolute energy scale in most cases accurate to within 0.3 eV for sulfur compounds with the calibration of the XANES spectra as used in this thesis.\textsuperscript{47}

All transition energies and intensities for the theoretical sulfur K-edge XANES spectra presented in this thesis were computed with the transition potential (DFT - TP) method,\textsuperscript{24} implemented in the StoBe-deMon DFT program system,\textsuperscript{48} using non-local exchange and correlation functionals throughout.\textsuperscript{45} In short, the orbitals for the molecular species are determined using a high quality molecular basis set with a half occupied core orbital at the excitation site, i.e. the potential used for the excited states is derived by removing half an electron from the sulfur atom 1s orbital. The description of the unoccupied orbitals corresponding to the Rydberg and continuum states is improved by a large set of diffuse basis functions that are added in the second step of the calculation on the excited sulfur atom (also known as the “double basis set technique”).\textsuperscript{49} The transition moments were calculated as the dipole matrix element between the initial and final state describing both states with the same set of orbitals.\textsuperscript{24} Two more corrections need to be accounted for, namely the relativistic and relaxation effects, respectively, applied to all the computed states to obtain the absolute energy of the transitions. Since the starting point in all the simulations within the program is the
non-relativistic Schrödinger equation, the description of the systems becomes less valid when the velocity of particles approaches the speed of light. Therefore, to describe more accurately the inner electrons, corrections due to the relativistic effects on the S(1s) ionization potential (IP) were calculated for atomic sulfur at the MCPF level (Modified Coupled Pair Functional) using first-order perturbation-theory corrections including the mass-velocity and Darwin terms. This effect increases the calculated S(1s) IP by 7.4 eV and is applied as an overall shift of the energy scale of the spectrum. The final state relaxation effects for several of the first excited states were computed state-by-state in Δ(Kohn-Sham) calculations through a variational treatment allowing full relaxation of the core excited state. The absolute energies obtained in this way for our studied systems showed satisfactory agreement with the experimental spectra, except for a few highly charged anionic species.

The calculated transitions, described by their energy and oscillator strength, are convoluted with Gaussian functions to mimic the experimental broadenings of the XANES features. Thus, a certain full width at half maximum (FWHM) was chosen to match the experimental broadening for the region below the ionization potential (IP), then the FWHM of the Gaussian was linearly increased to 8 eV over the next 20 eV, and then kept constant at 8 eV to simulate the approach towards continuum at higher energies and guarantee that no spurious, basis set dependent resonances occur in the continuum. The low energy spectral features in that calculated XANES spectrum could then be directly compared with the experimental one. The broadening values used for convolutions account for different experimental factors which affect the energy resolution, such as instrumental broadening (~0.5 eV), vibrational excitations and lifetime broadening as well as broadening due to hydrogen bonding and symmetry breaking vibrational and surrounding effects. Thus, for the excitation of the electron to bound states (below the IP), the vibrational, experimental and lifetime broadening contribute to the observed FWHM, while for the transitions above the IP (into continuum states), the short lifetime of the excited electron as well as the density of states smear the features. The larger broadening applied to continuum states above the edge compensates for the discrete sampling of the kinetic energies that is inherent with the use of a local Gaussian type basis. Therefore, the increase in the broadening above the continuum is justified and gives reasonable results. Note that the discrete representation of the continuum can be made denser allowing a smaller broadening to be applied either by adding the augmentation basis also to surrounding centres, or using sum of contributions from several surrounding structures, especially in the case of species in solution.

The orbital and auxiliary basis sets used in the computations are described in the manuscripts. For compounds that contained more than one sulfur
atom, effective core potentials (ECP) which eliminate the S(1s,2s,2p) orbitals were used for all sulfur atoms except for the core-excited one, thus simplifying the description of the core hole.\textsuperscript{52} To simulate the effect of hydrogen bonding in aqueous solutions, several water molecules were included in the models, setting the distance O_{entity}⋯O_{water} to 2.75 Å and the bond angle in the water molecules to 105 degrees.
4 Results and discussion

4.1 DMSO solvated metal ions

4.1.1 Crystal structure of octakis(dmso)lanthanoid(III) iodides

The prediction from Pearson’s rules\textsuperscript{26} that the hard lanthanoid(III) ions would prefer to coordinate dimethyl sulfoxide ligands through the oxygen atoms has been confirmed without exception in many studies.\textsuperscript{VIII, IX,53-62} The determination of the crystal structures for the series of [M(OS(CH\textsubscript{3})\textsubscript{2})\textsubscript{8}]I\textsubscript{3} compounds (M = La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Lu) revealed that all the fully solvated trivalent lanthanoid ions are ligated with eight dimethyl sulfoxide solvent molecules in a distorted square antiprismatic configuration, \textit{cf.} Figure 12.\textsuperscript{VIII} The crystal structure shows discrete [M(OS(CH\textsubscript{3})\textsubscript{2})\textsubscript{8}]\textsuperscript{3+} entities and iodide ions; for the latter the closest C(-H)…I contacts to the methyl hydrogen atoms of the ligand molecules are at about 3.9 Å. The larger lanthanum(III), cerium(III) and praseodymium(III) ions crystallize in the orthorhombic space group \textit{Pbca} (No. 61) with \( Z = 8 \), while all the remaining investigated lanthanoid(III) ions were described in the monoclinic space group \textit{P\textsubscript{2}1\textsubscript{1}/n} (No. 14) and \( Z = 4 \). All the solvates contain up to three disordered ligand molecules, each of them located in two different orientations related by a twist around the metal-oxygen (M-O) bond (\textit{cf.} Table 3).

The commonly used way to describe disordered dimethyl sulfoxide ligands with two partially occupied sulfur positions,\textsuperscript{63} may provide unreliable M-O bond distances due to the high displacement parameters obtained for the often unresolved sites of the oxygen and carbon atoms. A semi-rigid model with complete dimethyl sulfoxide molecules in two alternative sites was introduced, which reduced these inconsistencies and allowed the positions of all closely situated, partially occupied atomic sites to be resolved. Several constraints were imposed during the refinements on the S-C, O-S, C···C and O···C bond distances of the disordered ligands while refining their site occupancy factors and atomic positions. The new model has been employed also on the previously measured data of the monoclinic octakis(dimethyl sulfoxide)yttrium(III) iodide structure to refine the bond distances and angles.
The octakis(dimethyl sulfoxide)lanthanum(III) complex at 100 K in the [La(OS(CH$_3$)$_2$)$_8$I$_3$] crystal structure with 40% probability ellipsoids. Three of the dimethyl sulfoxide ligands are disordered and described with semi-rigid molecular models in two alternative positions.

Figure 12. The octakis(dimethyl sulfoxide)lanthanum(III) complex at 100 K in the [La(OS(CH$_3$)$_2$)$_8$I$_3$] crystal structure with 40% probability ellipsoids. Three of the dimethyl sulfoxide ligands are disordered and described with semi-rigid molecular models in two alternative positions.

The gradual change in ionic size along the lanthanoid(III) series, with the same electron configuration of the outer valence shell of all the ions, provides a unique opportunity to systematically study trends in chemical bonding and coordination chemistry related to hard and highly charged metal ions. As expected, the mean M-O bond distances in the [M(OS(CH$_3$)$_2$)$_8$]$^{3+}$ complexes decrease smoothly as the atomic number increases, cf. Table 3. For all studied lanthanoid(III) ions, the individual M-O bond distances show a rather broad distribution ($\pm$0.05 Å) with their mean M-O bond distances similar to other reports for dimethyl sulfoxide solvated lanthanoid(III) ions. Thus, the mean La-O, Pr-O and Gd-O bond distances of 2.49, 2.44 and 2.38 Å, respectively, obtained in this study are despite the disorder close to previously reported values of 2.49, 2.39 and 2.45 Å.$^{54,57,59}$ In addition, data collected at 100 K for the [M(OS(CH$_3$)$_2$)$_8$I$_3$] compounds, M = La and Nd, showed no change in their mean M-O bond distances from room temperature.
Table 3. Crystallographic occupancy factors in % (estimated standard deviation ±1%) for disordered dimethyl sulfoxide (Me$_2$SO) ligands in the [M(OSMe$_2$)$_8$I$_3$ (M = La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Lu and Y) compounds at ambient temperature (for La and Nd also at 100 K). The mean bond distances and angles are given in Å and degrees, respectively.

<table>
<thead>
<tr>
<th>M</th>
<th>Occupancy factors for S, O and C (%)</th>
<th>M-O$^a$ distance</th>
<th>MOS$^b$ angle</th>
<th>S-O$^b$ distance</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Me$_2$SO(1) Me$_2$SO(2) Me$_2$SO(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(100K)</td>
<td>53/47 85/15 85/15</td>
<td>2.49</td>
<td>135.8</td>
<td>1.52</td>
</tr>
<tr>
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<td>61/39 60/40</td>
<td>2.49</td>
<td>138.3</td>
<td>1.50</td>
</tr>
<tr>
<td>Ce</td>
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<td>2.47</td>
<td>137.5</td>
<td>1.50</td>
</tr>
<tr>
<td>Pr</td>
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<td>2.44</td>
<td>136.7</td>
<td>1.49</td>
</tr>
<tr>
<td>Nd(100K)</td>
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<td>2.43</td>
<td>133.3</td>
<td>1.53</td>
</tr>
<tr>
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<td>63/37 52/48 53/47</td>
<td>2.43</td>
<td>137.0</td>
<td>1.49</td>
</tr>
<tr>
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<td>2.40</td>
<td>134.6</td>
<td>1.50</td>
</tr>
<tr>
<td>Gd</td>
<td>51/49 68/32 81/19</td>
<td>2.38</td>
<td>133.1</td>
<td>1.50</td>
</tr>
<tr>
<td>Dy</td>
<td>84/16 72/28 54/46</td>
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<td>133.2</td>
<td>1.51</td>
</tr>
<tr>
<td>Er</td>
<td>79/21 55/45</td>
<td>2.34</td>
<td>131.8</td>
<td>1.50</td>
</tr>
<tr>
<td>Lu</td>
<td>83/17 41/59</td>
<td>2.30</td>
<td>131.4</td>
<td>1.51</td>
</tr>
<tr>
<td>Y</td>
<td>77/23 53/47 89/11</td>
<td>2.34</td>
<td>132.3</td>
<td>1.52</td>
</tr>
</tbody>
</table>

$^a$ The mean MO bond length and mean MOS angle were obtained considering the occupancy.

$^b$ The mean S-O bond distance was calculated including only the ordered ligands.

Even though the accuracy of the mean MOS angle is limited because of the disorder, there is a generally decreasing trend from about 138° for La to 131° for Lu (Table 3). A decrease in the MOS angle usually indicates a stronger M-O bond,$^{64}$ in this case consistent with the decreasing ionic radii. The MOS angles are smallest for the heaviest rare earth ions as expected from the increasing polarization of the shorter M$^{III}$-O bonds.

As illustrated in Figure 13, the cell volume per metal atom follows a linear correlation vs. the mean bond distance for both the series of monoclinic and orthorhombic [M(OS(CH$_3$)$_2$)$_8$I$_3$ crystal structures. However, it is evident that the molecular packing is more efficient in the orthorhombic system for M = La, Ce and Pr, which have smaller cell volumes than that for the monoclinic [Nd(OS(CH$_3$)$_2$)$_8$I$_3$ compound despite longer M-O bonds and larger MOS angles. The larger number of distorted ligand molecules found in the monoclinic structures (Table 3) seems to be related to their less efficient packing.
Figure 13. Unit cell volumes per metal ion in the \([\text{M(OS(CH}_3)_2}_8]\)\(3^+\) crystal structures vs. the mean M-O bond distances illustrates a break at the phase transition with less efficient packing for the smaller ions in the monoclinic structures.

4.1.2 EXAFS studies of \([\text{M(dmso)}_{8}]^{3^+}\) complexes in solution and in the solid state

The structures in solution of the \([\text{M(OS(CH}_3)_2}_8]\)\(3^+\) complexes of most lanthanoid(III) ions have been investigated by extended x-ray absorption fine structure (EXAFS) spectra, collected at L\(_3\)- and in some cases K-edges, and compared with corresponding EXAFS measurements and results for the solid iodides.\(^{I IX}\) Previous reports for lanthanoid(III) ions in other oxygen donor solvents, i.e. water, \(N,N\)-dimethylformamide, \(N,N\)-dimethylacetamide, \(N,N'\)-dimethylpropylene urea, have indicated a change in coordination number of the solvated lanthanoid(III) ions along the lanthanoid series.\(^{65-67}\) One aim of the current study was to examine if such a change would occur for the dimethyl sulfoxide solvated lanthanoid(III) ions in solution. For that purpose, the mean M-O bond distances determined from EXAFS data for dimethyl sulfoxide solutions were directly compared to those obtained from EXAFS determinations of the solid \([\text{M(OS(CH}_3)_2}_8]\)\(3^+\) compounds.\(^{VIII}\) Such a comparison is more reliable than with crystallographic distances, because EXAFS is a lattice-independent structural method and the mean M-O bond distances extracted from EXAFS data are not affected by the presence of disordered ligands in the crystalline phase. Also, for large and/or asymmetric distributions of the M-O bond distances the mean value from EXAFS is weighted differently than the arithmetic average for the crystallographic distances.

Even qualitative comparisons of the raw EXAFS spectra of some \([\text{M(OS(CH}_3)_2}_8]\)\(3^+\) solvates in the solids and solutions, which are very similar as shown in Figure 14, strongly suggest similar coordination, namely that all the lanthanoid(III) ions are coordinated by eight dimethyl sulfoxide mole-
cules. This conclusion is also confirmed by the results obtained through detailed data analyses. However, there are different complications, in particular for the EXAFS measurements at the L$_3$-edge for the lighter elements of this series, which affect the data quality in the data collection and evaluation procedures. Special concerns are e.g.:

- The high absorption of the dimethyl sulfoxide solutions at low energies, which makes fluorescence (Lytle) detection necessary. Fluorescence from the iodide anions were then, by means of a more energy-discriminating Ge-detector, found to contribute to the background, which made splining to extract the EXAFS oscillations difficult and increased the noise level in the data.
- Double electron excitations causing extra “peaks” (actually extra absorption edges) in the EXAFS oscillations are frequent for the lanthanoid ions (see e.g. the feature at $k \sim 6$ Å$^{-1}$ for the La L$_3$-edge in Fig. 14), and should be handled properly in the data treatment.
- So called “glitches” cause other peaks in the data. Those are due to sudden jumps in the incident beam intensity $I_0$ by double reflections from the monochromator that frequently occur in the low-energy range for the Si(111) and Si(220) monochromator crystals normally used. For the monochromators available at SSRL the energies and intensities are described in a glitch library (http://www-ssrl.slac.stanford.edu/~xas/glitch/glitch.html), and different cuts of the Si(220) crystals were selected for our different lanthanoid samples to reduce those disturbances.
- The onset of the L$_2$-edge limits the useful L$_3$ EXAFS $k$-range especially for the lighter elements, e.g. for La $k_{\text{max}} \approx 9$ Å$^{-1}$. The restricted range limits the $R$-space resolution ($\Delta R \approx \pi / 2 \Delta k$, where $\Delta k$ is the $k$-range), which especially for a broad distribution of M-O distances restricts accuracy and also testing for asymmetry in the distribution.
- Data collection at the K-edge that was performed for some of the samples. The high energies reached at the beamline BM29 at ESRF, Grenoble, are extreme for EXAFS measurements; the K-edge for Lu appears at 63.3 keV. The core hole life-time is then very short, which reduces the interference between the outgoing photoelectron wave and the wave backscattered from surrounding electrons. The effect is a damping of the EXAFS oscillations that can be expressed as a change of the mean free path factor, $\exp[-2R_j / \Lambda(k)]$, in the simplified EXAFS equation (cf. equation (1)).

The corrections for the core hole life-time effect were performed by Prof. D’Angelo, see paper IX. Advantages of the high-energy K-edge measurements are the absence of double excitations, monochromator glitches, high
absorption problems or $k$-range limitations; on the other hand the signal-to-
noise ratio turned out to become fairly low at high $k$ after the corrections
(Fig. 14). However, especially for La the K-edge data were a useful com-
plement to the $L_3$ edge measurements.

Thus, not only the experimental data collection had complications, but
also the data evaluation. Comparisons of data analyses performed in differ-
ent ways with program systems based on different principles and with differ-
ent options available (e.g. asymmetric distributions of distances, removal of
double excitations) were used for testing the reliability and accuracy of the
model calculations. The final results were found to well reproduce the ex-
perimental spectra for all the samples investigated (Fig. 15 and paper IX).

Data analyses were carried out by means of both the GNXAS and EXAF-
SPAK program systems and the refined structural parameters for the models
used are reported in paper IX. The GNXAS program could model an asym-
metric distribution of the ion-oxygen distances and the centroid of that dis-
tribution therefore allowed a more reliable comparison with the average of
the M-O distances obtained from the crystallographic study on the solid sol-
vates. Refinements were also performed without allowing for asymmetry
in the GNXAS program; the results could then be compared to those from EXAFSPAK, that does not include an option for describing asymmetric distributions. Beside accounting for asymmetry, the GNXAS program can also handle multiple scattering and double excitations in a more rigorous way than EXAFSPAK. For both the solids and solutions investigated, the changes induced in the mean M-O bond distances when allowing for asymmetry were rather small (<0.01 Å), which suggest that the distributions are fairly symmetrical (cf. Table 1, paper IX). With a few minor exceptions, the mean M-O bond distances obtained from the EXAFS data for both solid and solution samples are also in satisfactory agreement with the average values obtained from crystallography, cf. Table 4, even though no meaningful comparisons could be performed of the uncertain mean MOS angles obtained from the EXAFS refinements.

As expected for the lanthanoid series, the M-O bond distances decrease monotonically with the atomic number. However, the decrease is faster than predicted from the tabulated ionic radii for eight-coordination (cf. Table 4).\textsuperscript{68} This deviation increases along the series from La to Lu without any indication of a coordination number change. Thus, the increase in the polarization of the M-O bonds with shrinking size from the lightest to the heaviest lanthanoid(III) ions appears to reduce the oxygen ionic radius. A combined XANES and vibrational spectroscopic study was then undertaken to investigate this phenomenon.
Table 4. Mean M-O bond distances from EXAFS results for solid [M(OS(CH$_3$)$_2$)$_8$]I$_3$ compounds and of lanthanoid(III) ions in dimethyl sulfoxide solution, compared with values from the crystallographic study. The differences between the M-O bond distances in this study and those obtained from Shannon’s M(III) ionic radii (IR) in eight-coordination (Ref. 68) combined with the O-radius 1.34 Å, are given.

<table>
<thead>
<tr>
<th></th>
<th>EXAFS Solid</th>
<th>EXAFS Solution</th>
<th>Crystal Structure</th>
<th>Ionic radii (IR)</th>
</tr>
</thead>
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<td></td>
<td>d/Å</td>
<td>d/Å</td>
<td>d/Å</td>
<td>IR$^{Shannon}$</td>
</tr>
<tr>
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<td>2.385</td>
<td>2.38</td>
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<td>2.367</td>
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<td>2.29</td>
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</tbody>
</table>

4.1.3 Vibrational spectroscopy on [M(dmso)$_8$]$^{3+}$ complexes

The solid [M(OSMe$_2$)$_8$]I$_3$ compounds were favourable for vibrational spectroscopic studies on the [M(OSMe$_2$)$_8$]$^{3+}$ complexes, because the iodide ions do not provide additional vibrational bands in the Raman and IR spectra, as e.g. perchlorate or trifluoromethanesulfonate anions would. Qualitatively, the direction of the shift of the S-O stretching frequency in the IR spectrum of dimethyl sulfoxide solvates can distinguish whether the dimethyl sulfoxide ligand coordinates a metal ion through its oxygen or sulfur atom.$^{69}$ As expected from the crystal structures, this band was downshifted with regard to the frequency found for the dimethyl sulfoxide monomer for all the [M(OSMe$_2$)$_8$]$^{3+}$ complexes investigated.$^VIII$ Otherwise, the most significant change observed in the vibrational spectrum is the appearance of a few new bands due to the M-O coordination and some shifts of the ligand skeletal modes.

The interpretation and assignment of the large number of frequencies observed in the vibrational spectra is not straightforward, because of overlap-
The assignment of the vibrational bands for all the skeletal normal modes of the octakis(dimethyl sulfoxide)lanthanoid(III) solvates has been acquired through comparison with the experimental spectra of liquid dimethyl sulfoxide, supported by results from the normal coordinate analyses (cf. Table 4, paper VIII).

The highest possible point group symmetry for the \( [M(\text{OSMe}_2)_8]^{3+} \) complexes is \( D_{4d} \), when describing the methyl groups as point masses, which gives rise to \( (3N-6) = 93 \) normal vibrational modes. These modes belong to \( 7A_1 + 4A_2 + 5B_1 + 7B_2 + 12E_1 + 12E_2 + 11E_3 \) symmetry species, where \( A_1, E_2 \) and \( E_3 \) should be only Raman-active, while \( B_2 \) and \( E_1 \) should be only IR-active, and the \( A_2 \) and \( B_1 \) modes inactive in IR and Raman vibrational spectra.

The S-O stretching bands in the lanthanoid series of \( [M(\text{OSMe}_2)_8]^{3+} \) complexes are found just below 1000 cm\(^{-1}\). In Raman, the \( A_1, E_2 \) and \( E_3 \) symmetry species corresponding to this vibrational mode occur in the region 958-966 cm\(^{-1}\), while the \( B_2 \) and \( E_1 \) symmetry species active in IR appear in the 970 - 939 cm\(^{-1}\) range. The assignments of vibrational frequencies to the \( \text{CH}_3/\text{SC}_2 \) stretching and deformation modes of the dimethyl sulfoxide ligands are given in Tables 4 and S-5 (paper VIII). These modes were affected by deuteration and also downshifted upon coordination, with the largest shift for the C-S stretchings.

The vibrational frequencies corresponding to the M-O bonds for the \( [M(\text{OSMe}_2)_8]^{3+} \) complexes (\( M = Y, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er} \) and \( \text{Lu} \)) appear in the region 400 - 450 cm\(^{-1}\). As expected, the M-O stretching frequencies increase smoothly with the gradual decrease of the size of the central metal ion. The averaged M-O stretching frequency, \( \tilde{\nu} = (\nu_{A_1} + \nu_{B_2} + 2\nu_{E_1} + 2\nu_{E_2} + 2\nu_{E_3})/8 \) (the total number of MO stretchings is 8), which is recommended for use in qualitative correlations, \(^{64,70,71}\) increases from 408 to 432 cm\(^{-1}\) from \( [\text{La(OSMe}_2)_8]^{3+} \) to \( [\text{Lu(OSMe}_2)_8]^{3+} \), reflecting the effect of the decrease in M-O bond distance along the lanthanoid(III) series.

Due to the coupling of different vibrational modes influencing in particular the M-O frequencies, it is more satisfactory to correlate their corresponding force constants, instead of frequencies of certain modes, with the properties of the bonds. As mentioned in section 2.1.4, one should keep in mind that there is in principle no simple relation between force constant and bond strength; however, comparisons within groups of related complexes can provide useful information.

As illustrated in Figure 16, the calculated M-O and S-O force constants correlate almost linearly with the M-O bond distances, except at the change in space group symmetry from monoclinic to orthorhombic between \( \text{Pr} \) and \( \text{Nd} \). A decrease of 7% in the mean M-O bond distance from \( \text{La} \) to \( \text{Lu} \), for the octakis(dimethyl sulfoxide) lanthanoid(III) iodides, has produced an increase
of the corresponding force constant by 5%. On the other hand, the force constants corresponding to the S-O and S-C stretching modes change only 3.2% and 1.7%, respectively (Table 5, paper VIII).

The overall change in the MO stretching force constant for the octa-coordinated dimethyl sulfoxide solvates is significantly smaller than the corresponding force constant change found for the nona-hydrated lanthanoid(III) trifluoromethanesulfonate compounds. Thus, for these hydrated complexes the M-O bond distances, in the trigonal MO$_6$ prism and in the capping positions, decrease from La to Lu by 9% and 4%, respectively, which leads to an increase in their corresponding force constants by 43% and 33%. The smallest ions, Yb$^{3+}$ and Lu$^{3+}$, deviate from this trend due to the increased ligand-ligand repulsion that leads to water deficit in the capping positions.

The stronger steric repulsion between the ligands in the dimethyl sulfoxide complexes than in the hydrates probably explains the relatively small increase in the MO force constants for the dimethyl sulfoxide solvates. Figure 16 shows that with the tighter packing for the monoclinic systems (M = Nd to Lu) the increase in the force constants becomes lower.

Figure 16. Force constants for (left) M-O and (right) S-O stretchings vs. mean M-O bond lengths for the dimethyl sulfoxide solvates [M(OSMe$_2$)$_8$]I$_3$.

Correlations between the M-O force constants and mean bond lengths for the complexes of the lanthanoid(III) ions with dimethyl sulfoxide and water ligands, respectively, as well as for the octahedral hexakis(dimethyl sulfoxide) solvates of scandium and Group 13 metal ions are shown in Fig. 17. It clearly illustrates that in spite of the similar M-O bond lengths the force constants for the eight-coordinated dimethyl sulfoxide complexes are much higher than for nine-coordinated lanthanoid(III) aqua ions. This suggests that dimethyl sulfoxide binds much stronger to the lanthanoid(III) ions than wa-
ter molecules, a conclusion strengthened by crystallography results for mixed ligand complexes. The mean M-O(DMSO) distances found for the [Ce(OSMe$_2$)$_6$(H$_2$O)$_2$]$^{3+}$ and [Y(OSMe$_2$)$_2$(H$_2$O)$_6$]$^{3+}$ solvates are much shorter than the average M-O(H$_2$O) distances to the water molecules and the corresponding M-O(DMSO) distances determined for the fully octasolvated complexes. The mean Ce-O(DMSO) and Ce-O(H$_2$O) bond distances reported for [Ce(OSMe$_2$)$_6$(H$_2$O)$_2$]$^{3+}$ complex were found to be 2.447 Å and 2.517 Å, respectively. For the [Y(OSMe$_2$)$_2$(H$_2$O)$_6$]$^{3+}$ solvate, the mean Y-O(DMSO) and Y-O(H$_2$O) bond distances were re-evaluated with the new restrained model, which yielded 2.272 Å and 2.38 Å, respectively.

For the oxygen-coordinated hexakis(dimethyl sulfoxide) solvates of Sc(III) and the Group 13 ions, the $K$(MO) force constants decrease continuously from Al to In with increasing M-O bond length. The corresponding solvate of the trivalent thallium ion shows an obvious deviation from this trend reflecting the more covalent character of the Tl-O bonds that is demonstrated by the unexpectedly high M-O and S-O stretching force constants despite longer M-O and S-O bond distances.

![Figure 17. M-O force constants vs. M-O bond distances](image)

**Figure 17.** M-O force constants vs. M-O bond distances for a) [M(OSMe$_2$)$_6$]$^{3+}$ complexes, M = Al, Ga, In, Tl and Sc (▲); b) [M(OSMe$_2$)$_8$]$^{3+}$, M = La, Ce, Pr, Nd, Gd, Tb, Dy, Er, Lu (□) and Y(■); c) [M(H$_2$O)$_9$]$^{3+}$ complexes, M = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu for trigonal prism (Δ) and d) capping (○) M-O.

### 4.1.4 XANES spectroscopy on dimethyl sulfoxide solvates

**Hexakis(dimethyl sulfoxide)metal solvates** [M(OSMe$_2$)$_6$]$^{3+}$. The dimethyl sulfoxide molecule has been studied free (in dilute acetonitrile solution) and
as a ligand by means of experimental sulfur K-edge XANES spectra, with
the interpretations aided by theoretical DFT calculations. The oxygen-
coordinated hexakis(dimethyl sulfoxide)solvates of the trivalent metal ions
of Group 13, Al, Ga, In and Tl, and of Group 3, Sc, exhibit similar sulfur K-
edge XANES spectra.\textsuperscript{II,IX} They show larger splitting and a different intensity
distribution of the features within the main asymmetric peak than for the
uncoordinated DMSO molecule (cf. Fig. 18). These changes induced through
coordination were investigated by means of theoretical DFT calculations
allowing the experimental features to be assigned and interpreted.\textsuperscript{II}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure18}
\caption{Experimental sulfur K-edge XANES spectra (normalized intensities) of
the octahedral M(dmso)\textsubscript{6}\textsuperscript{3+} complexes of the group 13 metal ions (from the top M =
Tl, In, Ga and Al), and of 50 mM dimethyl sulfoxide in acetonitrile. The calculated
spectra for free dimethyl sulfoxide molecules, C1 with assumed S-O distance 1.595
Å and C2 with 1.495 Å, are illustrated together with the vertical bars which corre-
spond to the calculated energies and cross-sections for the x-ray induced excitations
of the sulfur 1s electron for free dimethyl sulfoxide, and for interactions between the
oxygen atom and a point charge P\textsuperscript{+} or a Mg\textsuperscript{2+} ion. The definition of the contributions
a, b, c and d is given on page 38.}
\end{figure}

Theoretical sulfur K-edge XANES spectra were computed for the free di-
methyl sulfoxide molecule in C\textsubscript{s} point group symmetry. The effect of a
variation in the S-O bond distance was studied for two different S-O bond
distances, namely 1.495Å and 1.595 Å (C2 and C1, respectively, Fig. 18).
For oxygen-bonded solvates, the effects of electrostatic interactions were
simulated by a +1 point charge (P⁺), and interatomic orbital interactions be-
tween the dimethyl sulfoxide ligand and the metal ion were for computa-
tional reasons investigated by placing an Mg²⁺ ion at a distance of 2.0 Å
from the oxygen atom.

The shapes of the receiving MO:s for the main transitions within the
asymmetric peak in the experimental sulfur K-edge XANES spectrum of the
free dimethyl sulfoxide molecule have been visualized by the program
MOLEKEL (Fig. 19). Transition a corresponds to an MO with character of
antibonding σ*(S-O) plus sulfur lone-pair, b mainly antibonding π*(S-O),
and c antibonding σ*(S-O, S-C). The asymmetric peak splits further for the
octahedral M(dmso)₆³⁺ complexes. The splitting between two partly resolved
features increases from about 0.7 to 0.8 eV for Al, Ga, In (Fig. 18) and then
to 1.5 eV for the Tl(dmso)₆³⁺ solvate. The energy difference between the
calculated a and b transitions increases by about 1.5 eV, when coordinating
one dimethyl sulfoxide molecule to an Mg²⁺ ion (cf. Figure 18). A new tran-
sition d of relatively low intensity appears in the calculations at 2471 eV and
was assigned to a molecular orbital with charge transfer from sulfur to the
magnesium ion (cf. Figure 19). The calculated energy and corresponding
intensity for the a, b and c transitions are affected by the coordinating metal
ion and the character of the MO:s changes slightly.

The splitting of the features in the main experimental XANES peak is in-
duced by the coordination of the metal ions. The comparison in Figure 18
indicates that the influence of the M-O bond in the first place is to shift the
transition a toward low energy, while transitions b and c are less affected.
The receiving MO for a with antibonding σ*(S-O) character has for a cova-
lent interaction the bonding MO counterpart with σ(S-O) character. Increas-
ing atomic orbital overlap (or covalence) in the S-O bond would increase the
energy difference between that pair of MOs and shift the S(1s) transition a
toward higher energy. The charge difference between the O and S atoms increases
for an O-bonded dimethyl sulfoxide ligand. A strong and short bond to
M(III) ions should induce a σ-electron transfer O←S by increasing the sulfur
lone pair contribution in the σ(S-O) bond, strengthening the bond and in-
creasing the energy of the σ*(S-O) MO.

Thus, the observed energy shifts of transition a seem connected to the in-
creasing electrostatic polarization of the M(III)←O←S bonds expected for
the decreasing size of the Tl(III), In(III), Ga(III) and Al(III) ions of Group 13
that probably increases the contribution of the sulfur lone pair into the bond.
The additional lowering of the transition energy for the [Tl(dmso)₆]³⁺ com-
plex seems mostly to be an effect of the increasing degree of covalency and
also $\pi$-back bonding in the Tl(III)-O bonds, counteracting the lone pair contribution to the $\sigma$(S-O) bond.

Vibrational spectroscopy is another probe of changes in the metal ion-oxygen bonding, especially useful for dimethyl sulfoxide complexes when correlations can be made with the intramolecular S-O bonds. Previous analyses of the vibrational force constants for the dimethyl sulfoxide solvated trivalent ions show that the M-O stretching force constants $K_{S-O}/K_{M-O}$ (in N cm$^{-1}$) for the dimethyl sulfoxide solvates in Figure 18 are Al(III) 4.599/1.761, Ga(III) 4.168/1.617, In(III) 4.274/1.318 and Tl(III) 4.279/1.300.$^{64}$ Correlations between bond strength and force constant depend on the shape of the potential surface (section 2.1.4) and should be used with caution. While Al(III) with the highest energy of the $\sigma^*$ (S-O) molecular orbital also has the highest $K_{S-O}$ force constant, a comparison of the $K_{M-O}$ force constants shows that there are also covalent contributions to the M-O bonds, noticeable for the In(III) ion but especially prominent for the Tl(III) ion.

![DMSO and Mg$^{2+}$-DMSO](image)

Figure 19. The shapes of the MO:s corresponding to the transitions labeled in Fig. 18 for the free dimethyl sulfoxide molecule and for dimethyl sulfoxide coordinated to an Mg$^{2+}$ ion at a distance of 2.0 Å.

Octakis(dimethyl sulfoxide)lanthanoid(III) solvates [M(OSMe$_2$)$_8$]$^{3+}$. All the sulfur K-edge XANES spectra for the octakis(dimethyl sulfoxide)lanthanoid(III) complexes in this study show very similar shape (the spectra for La at the beginning and Lu at the end of the series are shown
below in Figure 20) with only slightly broader asymmetric absorption peaks than for unsolvated dimethyl sulfoxide molecules.

![Normalized sulfur K-edge XANES spectra of dimethyl sulfoxide solvated ions](image)

**Figure 20.** Normalized sulfur K-edge XANES spectra of dimethyl sulfoxide solvated ions: the hexasolvates of thallium(III) and scandium(III), the octasolvates of lutethium(III) and lanthanum(III), compared with uncoordinated (0.05 M) dimethyl sulfoxide in acetonitrile; the electronic transitions calculated for free dimethyl sulfoxide molecule are denoted $a$, $b$ and $c$ (paper II).

The vibrational force constants $K_{S-O}/K_{M-O}$ (in N cm$^{-1}$) for the dimethyl sulfoxide solvates displayed in Figure 20 are La(III) 4.545/1.432; Lu(III) 4.691/1.496; $^{\text{VIII}}$ Sc(III) 4.402/1.462,$^{71}$ and Tl(III), 4.279/1.300, while $K_{S-O}$ for a gaseous dimethyl sulfoxide molecule is 5.061 N cm$^{-1}$. For the La(III), Lu(III) and Sc(III) ions, which are of similar “hard” character, the lower S-O force constant for Sc(III) also corresponds to a lower energy of transition $a$, while no significant difference can be seen between the La and Lu XANES spectra (cf. Fig. 20).

The changes induced in the theoretical XANES spectrum by the pure electrostatic interactions between the dimethyl sulfoxide ligand and the point charge +1 (Fig. 18) shows that the main effect is some energy shifts of the $a$, $b$ and $c$ transitions and higher probability for transition $d$. The effect on the XANES spectra of the M-O bond when compared to that of gaseous dimethyl sulfoxide resembles such an electrostatic interaction. On the other hand, it seems that the splitting in the XANES spectra (decrease in the energy of the transition from S(1s) to $a$) generally increases for dimethyl sul-
foxide solvates with comparable types of metal ions when the $K_{S-O}$ value decreases.

**Protonated dimethyl sulfoxide, (CH$_3$)$_2$SOH$^+$.** The experimental sulfur K-edge XANES spectrum of the protonated dimethyl sulfoxide molecule, which is the dominating species in highly acidic solution, displays two resolved peaks with similar intensity and a shoulder on the high energy side. The features are centered at about 2472.9 eV, 2474.1 eV and 2475.3 eV, respectively, with the first peak appearing at lower energy than the asymmetrical peak observed for uncoordinated dimethyl sulfoxide (cf. Fig. 21).

![Figure 21](image)

**Figure 21.** Normalized sulfur K-edge XANES experimental spectra of dimethyl sulfoxide (0.05 M) in acetonitrile (solid line) and concentrated hydrochloric acid (dot-dashed line).

For the calculations of theoretical spectra the geometry of the protonated dimethyl sulfoxide molecule was obtained from the crystal structure determined by Jaswal and coworkers. Different models were constructed by adding one hydrogen bonded water molecule (H-O bond distances 1 Å and tetrahedral HOH angles) with the hydrogen bonding proton placed at 1.12 Å and 1.3 Å from the dimethyl sulfoxide oxygen atom, i.e. forming H$_3$O$^+$-OS(CH$_3$)$_2$ or H$_2$O-HOS(CH$_3$)$_2^+$ entities, respectively, while keeping the O-H$^-$O distance at 2.414 Å as in the crystal structure (Fig. 22). The theoretical spectra were calculated as described in section 3.2, applying corrections due to relativistic and relaxation effects as well as an additional empirical shift (−0.5 eV for model A and −0.6 eV for models B and C) to obtain coincidence between the energies for the main features in the experimental and theoretical spectrum.
Figure 22. Theoretical S K-edge XANES spectra (solid lines) calculated for the unsolvated protonated dimethyl sulfoxide molecule, model A, solvated with one hydrogen bonded water molecule $\text{H}_2\text{O}^+\cdots\text{HOS(CH}_3)_2$, model B; and $\text{H}_2\text{O}^-\cdots\text{OS(CH}_3)_2$, model C, compared with the experimental spectrum of 0.05 M dimethyl sulfoxide in concentrated hydrochloric acid (dot-dashed line). The vertical bars represent the calculated transition energies and cross-sections, convoluted with 0.9 eV (model A) and 1.1 eV (models B and C) FWHM Gaussians below 2476.2 eV, linearly increasing to 8 eV FWHM above 2496.2 eV. The shapes of the unoccupied molecular orbitals corresponding to 1, 2, 3 and 4 are shown in Figure 23.
Figure 23. Shapes of the unoccupied molecular orbitals for the protonated dimethyl sulfoxide molecule corresponding to transitions 1, 2, 3 and 4 in Fig. 22 for model A, and (below) transitions 1, 2 and 3 for the models B and C.

The two experimental spectral features at about 2472.9 eV and 2474.1 eV are reproduced by transitions 1 and 2 for all three models. The splitting between these states decreases gradually, from 1.6 eV (A), 1.2 (B) to 1.1 eV (C), mostly because the 2nd state shifts toward lower energy. The experimental shoulder corresponds to transition 3 for models B and C, and to 3 and 4 for model A. In the theoretical spectra for all three models state 1 is attributed to the transition from S(1s) to antibonding σ*(S-O), and transition 2 to an MO with π*(S-O) bond character. The main difference in the transition energies and intensities is found for the unhydrated model A, where states 3 and 4 are attributed to MOs with σ*(O-H) character and σ*(S-O, S-C) contribution from the two methyl groups. State 3 for model B, mainly with σ*(S-O, S-C) character, resembles state 4 for model A (cf. Fig. 23). The shape of the MOs for the main transitions for models B and C are also similar to those for the uncoordinated DMSO molecule.

The characters of the MO orbitals of states 1, 2 and 3 and the corresponding transitions are similar for the models B and C. The best match to the experimental spectrum is achieved for model B, even though models A and C also represent the main features satisfactorily. Thus, increasing the distance of the proton from the dimethyl sulfoxide oxygen atom only induces
small changes in the energy and intensity of the transitions, and the computed spectrum is not very sensitive to the position of the proton in the hydrogen bond.

4.2 The sulfite system – sulfonate and derivates

4.2.1 Crystal structures of sodium trichloromethanesulfonate monohydrate and deuterated cesium sulfonate

The structure and bonding for the sulfonate and substituted methylsulfonate anions were investigated by means of sulfur K-edge XANES spectra combined with DFT calculations and vibrational spectroscopy. VI The crystal structure of sodium trichloromethanesulfonate monohydrate (NaCCl₃SO₃·H₂O)\(^V\) was determined from single crystal diffraction data to be used in the comparisons. The compound crystallizes in the monoclinic space group \(P2_1/a\) with the pyramidal SO\(^3\) and CCl\(_3\) groups of the trichloromethanesulfonate (trichlate) anion linked via an S-C bond in staggered conformation with near \(C\(_{3v}\)\) symmetry (\(cf.\) Fig. 24). The S-O bond lengths are similar to those in the related triflate (CF\(_3\)SO\(_3\)) and methanesulfonate (CH\(_3\)SO\(_3\)) anions, but the S-C bond distance weakens and the O-S-O angles increase somewhat due to electron withdrawing effect of the electronegative chlorine and the steric repulsion between the CCl\(_3\) and SO\(_3\) groups, in particular when compared to the methanesulfonate anion. The water hydrogen atoms are involved in hydrogen bonding with the sulfonate oxygen atoms, one of them forming weak, bifurcated O-H...O hydrogen bonds to two different trichlate ions.

Figure 24. The structure of the trichlate CCl\(_3\)SO\(_3\)\(^-\) ion. The space-filling model, drawn with the van der Waals radii 1.81Å (Cl) and 1.40 Å (O), illustrates the steric repulsion between the CCl\(_3\) and SO\(_3\) groups, see Section 4.2.3.2.
The deuterated cesium sulfonate compound (CsDSO$_3$) was investigated by neutron powder diffraction$^\text{VI}$ in order to obtain the S-D bond distance. Neutron diffraction provides more accurate positions for the hydrogen atoms than x-rays, because of the relatively high scattering factor of the deuterium atom. Also, the positions of the atomic nuclei are obtained rather than the center of the electron density. This is due to the fact that neutrons are scattered by the atomic nuclei and with rather similar intensity for light and heavy atoms, while x-rays are scattered by the electrons with the scattering factors almost proportional to the number of electrons.

The S-D and S-O bond distances were obtained for the CsDSO$_3$ compound through Rietveld analysis of the neutron powder diffraction pattern (cf. Fig. 25). The initial structural parameters for the refinement were taken from the single crystal x-ray diffraction results of cesium sulfonate.$^\text{78}$ The crystal structure was used as model for the calculations of theoretical sulfur K-edge XANES spectra and for the normal coordinate analyses performed to assign the vibrational frequencies and evaluate the force constants for the sulfonate anion and its deuterated analogue.

![Figure 25. Observed (circles) and calculated (solid line) diffraction patterns of CsDSO$_3$. The deviations in the difference below are probably due to some hydrogen atom (H) contamination.](image)

4.2.2 XANES spectroscopy and DFT calculations

4.2.2.1 Sulfite system

The apparently simple and environmentally important sulfite system has been studied in different pH ranges by means of experimental sulfur K-edge XANES spectra aided by theoretical calculations.$^\text{VI}$ In highly acidic sulfite solutions ($\text{pH} < \sim 1$) the hydrated SO$_2$\text{(aq)} species dominates, while in the intermediate pH range ($4 < \text{pH} < 6$) two geometric isomers coexist, namely the hydrogen sulfite (SO$_3$H$^-$) and the sulfonate (HSO$_3^-$) ions (cf. Fig. 26). The hydrogen sulfite ion coordinates the hydrogen atom through one of the oxy-
gen atoms and has so far not been found in any crystal structure, while the structures of the cesium and rubidium sulfonates confirmed that the sulfonate anion has the hydrogen atom attached to the sulfur atom also in the solid state. More recently, studies carried out by means of $^{17}$O-NMR on aqueous sulfite solutions over a range of temperature, pH and concentrations provided evidence that the two isomers coexist in solutions and their isomerization equilibrium quotient ($Q_d = [\text{SO}_3\text{H}^-]/[\text{HSO}_3^-]$) was reported. In sulfite solutions with pH $> 9$ the sulfite ion ($\text{SO}_3^{2-}$), with $C_{3v}$ point group symmetry, prevails (cf. Fig. 26).

![Figure 26](image.png)

**Figure 26.** Fraction diagram showing the major species expected in 0.05 M sulfite(IV) solution at different pH values.

The sensitivity of sulfur K-edge XANES spectroscopy to the chemical bonding and environment around the sulfur atom is well exemplified for the various sulfite(IV) species, which have different geometrical arrangement around the sulfur atom and therefore significantly different XANES spectra (cf. Fig. 27a, b and c).

**Sulfur dioxide.** The experimental spectra of sulfur dioxide in the gas phase, $\text{SO}_2$ dissolved in acetonitrile, and in water (pH = 1.1), and of a 0.05 M $\text{Na}_2\text{SO}_3$ aqueous solution at pH = 0, are displayed together with the theoretical (gas phase) spectrum of the $\text{SO}_2$ molecule, Fig. 27. The XANES spectra corresponding to gaseous $\text{SO}_2$, and to $\text{SO}_2$ dissolved in acetonitrile (cf. Fig. 27e and f) are similar with sharp and well-resolved features, unlike the experimental spectra of the aqueous solutions (cf. Fig. 27c and d). The merging and increased broadening of the peaks observed in the spectra of the aqueous solutions are most likely due to the hydrogen bonds formed to $\text{SO}_2$, which are lacking in the non-hydrogen bonding solvent acetonitrile. The peak observed at about 2474 eV in the experimental spectrum of $\text{SO}_2$ dissolved in water at pH 1.1 (Figure 27d), absent for the other investigated solutions, is most likely due to the contribution of the hydrogen sulfite and sulfonate species present in about 10% at pH = 1.1 (cf. Fig. 26). These coexist-
ing species in the sulfite solutions at intermediate pH exhibit features at about 2474 eV, as illustrated in Fig. 27b.

The experimental features were assigned through comparison to the theoretical spectrum calculated by the DFT - TP method for the gas phase SO$_2$ molecule in the C$_{2v}$ point group. The calculated transitions marked in order of increasing energy (Fig. 27) are to:

1. the antibonding lowest unoccupied molecular orbital (LUMO) $\pi_g^*$ of symmetry species B$_1$;
2. LUMO+1 (A$_1$) characterized by in-plane $\pi^*$ mixing of oxygen 2p$_x$ and 2p$_z$ atomic orbitals;
3. LUMO+2 (B$_2$), representing the other oxygen 2p$_x$ and 2p$_z$ orbital combination;
4. LUMO+4 (B$_1$), a Rydberg dominated state with little valence character (cf. Appendix).

The LUMO+3 (A$_1$) at 2477.9 eV, dominated by $\sigma$-character with little p admixture, has very low intensity and is not visible in the experimental spectrum.$^\text{VI}$

Concluding, in strongly acidic solutions hydrated molecular sulfur dioxide, SO$_2$(aq), was the only detectable sulfur(IV) species.

![Figure 27. Sulfur K-edge XANES spectra](image)

**Figure 27.** Sulfur K-edge XANES spectra: a) Na$_2$SO$_3$(aq) at pH = 10.7; b) Na$_2$SO$_3$(aq) at pH = 3.9; c) Na$_2$SO$_3$(aq) at pH = 0; d) SO$_2$(aq) (4.5-5.5% in water); e) SO$_2$ dissolved in CH$_3$CN; f) SO$_2$(g); g) Theoretical SO$_2$ spectrum; calculated absorption energies and cross-sections (vertical bars) convoluted with a Gaussian function (FWHM) of 0.7 eV below the ionization threshold IP = 2477.35 eV, linearly increased to 8 eV up to about 2497 eV.

*Sulfite solutions at intermediate pH.* The experimental spectrum corresponding to the aqueous sulfite solution at pH = 3.9 (Fig. 28) exhibits features
from the two geometric isomers coexisting in this pH range. The theoretical spectra of these tautomeric species were computed to deconvolute the experimental spectrum, assign the electronic transitions and estimate the ratio of these species.

Since there is no crystal structure containing the hydrogen sulfite $\text{SO}_3\text{H}^-$ ion, its initial geometry was obtained by a theoretical optimization with GAUSSIAN98. However, the calculation for the isolated ion yielded an unreasonably long S-O bond distance (1.817 Å) for the S-O-H entity, similar to a previously reported value, but much longer than the other two S-O bond distances (1.51 Å). From the crystal structure of several hydrogen sulfate compounds, which contain the same type of S-O-H bond, this S-O(-H) distance was estimated to be usually about 0.1 Å longer than the S-O bond distances. As a result, the theoretical spectrum of this anion was computed for several models by gradually decreasing the S-O-H bond distance from 1.817 to 1.6 Å while keeping the other bond distances and angles unchanged. The value 1.6 Å gave the best agreement with the experimental spectrum (cf. Fig. 28A) and was used in the calculations.

The theoretical spectrum of the sulfonate ion (HSO$_3^-$) was calculated from the geometry obtained from the Rietveld refinement of the neutron powder diffraction pattern of the CsDSO$_3$ compound. The model and the theoretical spectrum for this species are illustrated in Fig. 28B.

A direct comparison of the theoretical spectra of these tautomeric ions with the experimental spectrum of 0.05 M Na$_2$SO$_3$(aq) at pH = 3.9, clearly shows that only the $\text{SO}_3\text{H}^-$ anion contributes to the first experimental peak (cf. Figs. 28A and 28B). The first experimental peak is generated by two electronic transitions separated by 0.42 eV; the MO corresponding to the first state $\textbf{1}$ (transition at 2474.8 eV) has antibonding $\sigma^*(\text{O-H})$ character, while the $\textbf{2}$nd transition takes place into a local $\sigma^*(\text{O-H})$ molecular orbital with Rydberg character (cf. Appendix). Some charge transfer from sulfur to the oxygen atoms of the hydrogen bonded water molecules is observed for both transitions. The most intense transitions calculated for the sulfonate anions marked in Fig. 28B were assigned as: for $\textbf{1}$ at about 2475 eV, S(1s)$\rightarrow$ $\sigma^*$ (H-S); for transition $\textbf{2}$ at 2478.5 eV the MO is attributed to a doubly degenerate E state with bonding $\pi$ character between the H and S atoms (cf. Appendix). This transition contributes partly to the $\textbf{2}$nd observed spectral feature and in the region about 2479 eV (cf. Figs. 28 A and 28B).
Figure 28. Theoretical S K-edge XANES spectra (solid line) for (A) SO$_3$H$^-$ ion with 3 hydrogen bonded water molecules and (B) hydrated (3 H$_2$O) HSO$_3^-$ ion compared with the experimental spectrum of 0.05 M Na$_2$SO$_3$ in aqueous solution at pH = 3.9 (dot-dashed line). The vertical bars represent the calculated transition energies and cross-sections, convoluted with FWHM Gaussians of 0.9/0.9 eV below 2474.9/2476.35 eV, linearly increasing to 8 eV FWHM above 2494.9/2496.35 eV, respectively. The unoccupied molecular orbitals corresponding to the marked transitions are described in the text.

The relative amount of the two isomeric species has been obtained by combining their corresponding theoretical spectra in different proportions. The best agreement with the experimental spectrum was achieved for the ratio SO$_3$H$^-$ : HSO$_3^-$ = 72:28, with an error limit estimated to ±5%, and is illustrated in Figure 29A. The equilibrium quotient ($Q_d = [SO_3H^+] : [HSO_3^-]$) value for the isomerization reaction was found to be 2.6 ± 0.5. This value is smaller than the one reported earlier ($Q_d = 4.9 ± 0.1$) from $^{17}$O NMR measurements that were carried out on solutions at 1.0 m ionic strength.  

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The temperature of the hydrogen sulfite solution at pH = 3.9 was varied to gain more information about the equilibrium of the two tautomeric species. As illustrated in Fig. 29B, when increasing the temperature to 70°C, the ratio of the first two peaks decreases and the intensity of the spectral features in the 2477-2481 eV region increases. These observations, in conjunction with the theoretical spectra, indicate that the amount of the sulfonate isomer is increasing with increasing temperature, consistent with the $^{17}$O NMR results.\textsuperscript{81}

In conclusion, our results confirm that both the hydrogen sulfite and sulfonate anions coexist in sulfite(IV) solutions at intermediate pH, with the hydrogen sulfite isomer dominating. The amount of the sulfonate species increased with increasing temperature in agreement with the NMR results of Horner and Connick.\textsuperscript{81}

**Figure 29.** (A) Theoretical S K-edge XANES spectrum for the hydrated SO$_3$H$^-$ (72%) and HSO$_3^-$ (28%) isomeric ions (solid line), compared with the experimental spectrum of 0.05 M Na$_2$SO$_3$ in aqueous solution at pH = 3.9 (dot-dashed line). The separate contribution of each ion is shown below. (B) Experimental sulfur K-edge XANES spectra of 0.05 M Na$_2$SO$_3$(aq) at pH = 3.9; temperature variation: 4 °C (dots), 25 °C (dot-dashed line), 70 °C (solid line).
The sulfite ion in solution and in the solid state. The sulfite ion, \( \text{SO}_3^{2-} \), is the major species in solution for pH > ~ 9 (cf. Fig. 26). Theoretical XANES spectra of the sulfite anion with its trigonal pyramidal \( C_3v \) structure have been computed for several models only differing in the number of explicitly added hydrogen bonded water molecules. The theoretical spectrum shown in Fig. 30 was calculated for the largest model comprising 21 water molecules around the sulfite ion. The large number of water molecules was required to distribute and stabilize the doubly negative charge of this ion, and to account for the hydrogen bonding in aqueous solutions. The hydrating water molecules were distributed as follows: six water molecules (\( 2^\text{nd} +2^\text{nd} \) hydration sphere) on each oxygen atom of the sulfite ion with the \( O \cdots O \) distance 2.75 Å, and the remaining three (\( 1^\text{st} +2^\text{nd} \)) were positioned above the sulfur atom with the \( S \cdots O \) distance 3.5 Å.

The main experimental features are satisfactorily reproduced by the theoretical calculations; the first peak at 2475.8 eV is generated by several transitions, however only 1 and 2 with highest cross section are assigned (cf. Fig. 30). They appear at 2475.4 eV and 2476.6 eV and the MO:s corresponding to these transitions display 3p lone pair character on the sulfur atom. The \( 2^\text{nd} \) experimental peak is also composite but the most intense transition 3, at 2477.9 eV, was attributed to \( S(1s) \rightarrow \sigma^*(S-O) \). Furthermore, both the transitions 1 and 3 show some charge transfer to the oxygen atoms of the surrounding water molecules (cf. Appendix).

![Figure 30. Sulfur K-edge XANES spectra of 0.05 M Na\(_2\)SO\(_3\)(aq) solution at pH = 10.7 (dots), solid Na\(_2\)SO\(_3\) (dashes), and the theoretical spectrum of the model with 21 water molecules around the sulfite ion (solid line), generated by convoluting the calculated transitions with 1.2 eV FWHM Gaussians below 2475 eV, linearly increasing to 8 eV FWHM at 2495 eV.](image-url)
4.2.2.2 Sulfonate (HSO$_3^-$) and substituted (X$_3$CSO$_3^-$) sulfonate anions

XANES of CsHSO$_3$ sulfonate. The changes induced in the experimental XANES spectra by connecting a proton to the lone pair of the sulfite ion were also examined. Both anions have trigonal pyramidal geometry with C$_{3v}$ symmetry. The most significant change is the absolute energy position of the first transition, which shifts about 2.3 eV higher for the sulfonate ion due to the shorter S-O bond distances. Some additional broad features are observed in the experimental spectra of both the sulfite and sulfonate ions, respectively.

The theoretical spectrum of cesium sulfonate was calculated for the model displayed in Fig. 31, which included four HSO$_3^-$ units and seven cesium cations. Even though the main peak at about 2478.1 eV could be reproduced reasonably well by one sulfonate entity, the model was extended, keeping C$_{3v}$ symmetry, in order to reproduce the shape resonances observed at 2481, 2485.7 and 2488 eV, respectively (cf. Fig. 31).

Figure 31. Experimental (dot-dashed line) S K-edge XANES spectrum of crystalline CsHSO$_3$, compared with the calculated spectrum (solid line) for the model in the inset. Convolution of the transitions was performed with 1.35 eV FWHM Gaussian functions below 2477.1 eV, linearly increasing to 8 eV FWHM after 2497.1 eV. The MO:s corresponding to transitions 1, 2 and 3 are described in the text.

The main experimental feature is explained fairly well by the corresponding peak in the theoretical spectrum. Several transitions contribute to that broad experimental peak, but only the three most intense have been assigned. The first two labeled states in Fig. 31 appear at 2477.1 and 2477.6 eV and have
A$_1$ symmetry, while transition $\mathbf{3}$ at 2478.7 eV is to a doubly degenerate E state. The MO:s corresponding to the states $\mathbf{1}$ and $\mathbf{2}$ have antibonding $\sigma^*(S-O)$ and $\sigma^*(H-S)$ bond character, respectively, while $\mathbf{3}$ is attributed to molecular orbitals with dominating $\pi$ bonding character between the H and S atoms and mixed antibonding $\sigma^* - \pi^*$ (S-O) bond character (cf. figures illustrated in Appendix).

The spectral peaks observed above 2480 eV were difficult to reproduce in the theoretical spectrum, even by the large model, and they seem to be transitions into Rydberg states, together with multiple-scattering effects enhanced by the long-range order in the structure.

*XANES of substituted $X_3$CSO$_3$ sulfonates ($X = H$, Cl, and F).* When substituting the hydrogen atom of the sulfonate with groups of different bonding character, significant changes may occur in their experimental XANES spectra (cf. Fig. 32). Replacing the hydrogen atom with a methyl group (cf. Figs. 32d and 32c) has little influence on the transitions because of the similar electronegativity of the H and CH$_3$ entities. On the other hand, substitution of the electron donating CH$_3$ group with the electron withdrawing CCl$_3$ and CF$_3$ groups influences the electronic transitions greatly. The main peak observed for the CsHSO$_3$ and NaCH$_3$SO$_3$ compound splits and the first feature shifts toward lower energy (cf. Fig. 32). The experimental spectra of the substituted sulfonates show the same trend in aqueous solutions.

![Normalized absorption](image)

**Figure 32.** Experimental S K-edge XANES spectra of the following solid compounds: sodium trifluoromethanesulfonate NaCF$_3$SO$_3$ (a), sodium trichloromethanesulfonate hydrate NaCCl$_3$SO$_3$·H$_2$O (b), sodium methanesulfonate NaCH$_3$SO$_3$ (c) and cesium sulfonate CsHSO$_3$ (d).

All the substituted sulfonates examined have the CX$_3$ and SO$_3$ groups in staggered C$_{3v}$ conformation (cf. Fig. 24). The models used to calculate their theoretical spectra were taken from corresponding crystal structures. One water molecule connected to each oxygen atom was used to describe the
hydrogen bonding expected to occur in aqueous solutions (cf. Figs. 33A, 33B and 33C). C$_{3v}$ symmetry of these anions was imposed during all the calculations.

The main peak at about 2478.4 eV in the experimental spectrum of the methanesulfonate ion CH$_3$SO$_3^-$ is generated by several transitions, but only 1, 2 and 3 of highest probability are specified (Fig. 33A). State 1, of A$_1$ symmetry appearing at 2478 eV, is attributed to S(1s) $\rightarrow$ $\sigma^*$ (S-C), while both 2, at 2478.2 eV, and 3, at 2478.7 eV, are doubly degenerate E states with corresponding MO:s of $\pi$ (S-C) bonding and antibonding $\pi^*$ (S-O) character, respectively (see Appendix).

The spectral features that appear at about 2476.8 eV (shoulder), 2477.9 eV and 2479.7 eV in the experimental spectrum of the trichlate ion (Fig. 33B) are rather well reproduced by the calculated electronic transitions. Again the first peak has several components. Transition 2 at 2477.4 eV, of A$_1$ symmetry and with highest cross section, corresponds to S(1s) $\rightarrow$ $\sigma^*$ (S-C). The MO corresponding to transition 1 of A$_1$ symmetry at 2476.7 eV, has antibonding $\sigma^*$ (C-Cl) character. The doubly degenerate E states, 3 and 4, separated by 0.66 eV, generate the 2nd experimental peak by excitation of the sulfur 1s electron into antibonding molecular orbitals of $\sigma^*$ (S-O) and $\pi^*$ (C-S) character, respectively (see Appendix).

Finally, the experimental spectra of the triflate ion in the solid state and in solution exhibit two partly resolved peaks within the range 2477-2479 eV and a broader resonance at about 2482.6 eV (Fig. 33C). In order to preserve C$_{3v}$ symmetry for the triflate anion, we used the mean bond angle and distance values of the four crystallographically independent configurations reported for the anhydrous hydrate by Sofina et al. Theoretical XANES spectrum calculated for this model for the triflate ion displays a single peak at about 2478.2 eV, which contains several components. The strongest contribution to this peak comes from transition 1, which is, as for the related methanesulfonate and trichlate ions, ascribed to an antibonding $\sigma^*$ (S-C) MO (Fig. 33C). The states denoted as 2 and 3 in Fig. 33C are doubly degenerate states corresponding to the shape resonance observed at 2482.6 eV. The MO:s corresponding to these transitions are all of antibonding $\pi^*$ (S-C)-character (cf. figures shown in Appendix).
Figure 33. (A) S K-edge XANES spectra of sodium methanesulfonate in 0.05 M aqueous solution (dots) and in the solid state (dot-dashed line). The theoretical spectrum (solid line) is obtained by convoluting the vertical bars with 1.1 eV FWHM Gaussian functions below 2476.2 eV, increasing to 8 eV FWHM after 2496.2 eV; (B) Experimental XANES spectra of NaCl$_2$SO$_3$·H$_2$O in the solid state (dots) and in 0.05 M aqueous solution (dashes) are displayed together with the theoretical spectrum (solid line) obtained by convoluting the calculated transitions (vertical bars) with 1.1 eV FWHM Gaussian functions below 2476.5 eV, linearly increased to 8 eV FWHM after 2496.5 eV. (C) Sulfur K-edge XANES spectra of NaCF$_3$SO$_3$ in the solid state (dots), and in 0.05 M aqueous solution (dashes). The theoretical spectrum (solid line) for the model with C$_{3v}$ symmetry in the inset was obtained by convoluting the calculated transitions with 1.1 eV FWHM Gaussian functions below 2476.7 eV, linearly increased to 8 eV FWHM after 2496.7 eV.
The regular \( C_{3v} \) model used to compute the theoretical spectrum of the triflate ion could not fully reproduce the splitting of the strongest observed feature in the 2477-2479 eV region. The theoretical spectra of the four independent configurations (cf. Table 5) in the crystal structure of anhydrous sodium triflate were then computed and are shown in Fig. 34. The same type of corrections were applied to the four structures, namely the relativistic effect (+7.4 eV), the relaxation effect of the first state calculated for the symmetrical model (-3.82 eV) and the additional empirical shift (+0.5 eV) as was applied for the symmetrical model.

![Figure 34](image)

**Figure 34.** *(top)* The theoretical K-edge XANES spectra calculated for four different configurations of the triflate ion (1, 2, 3 and 4) as reported by Sofina et al. (Ref. 84). *(bottom: 1-4)* The theoretical spectra are obtained by convoluting the vertical bars with 1.1 eV FWHM Gaussian functions below 2476.9 eV, increasing to 8 eV FWHM after 2496.9 eV.
Table 5. The bond distances and angles for the four independent configurations of the triflate ion as determined by Sofina et al. (Ref. 84). The values taken for the $C_{3v}$ symmetric model are mean values of the bond distances and angles of the four independent asymmetric triflate anions.

<table>
<thead>
<tr>
<th></th>
<th>Triflate 1</th>
<th>Triflate 2</th>
<th>Triflate 3</th>
<th>Triflate 4</th>
<th>$C_{3v}$ model</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-O distances</td>
<td>1.4218</td>
<td>1.4251</td>
<td>1.4298</td>
<td>1.4236</td>
<td>1.433</td>
</tr>
<tr>
<td>(Å)</td>
<td>1.4346</td>
<td>1.4310</td>
<td>1.4316</td>
<td>1.4312</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.4464</td>
<td>1.4392</td>
<td>1.4394</td>
<td>1.4432</td>
<td></td>
</tr>
<tr>
<td>OSO angles</td>
<td>113.15</td>
<td>112.48</td>
<td>112.30</td>
<td>112.52</td>
<td>113.9</td>
</tr>
<tr>
<td>(degrees)</td>
<td>114.44</td>
<td>112.85</td>
<td>114.61</td>
<td>113.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>115.02</td>
<td>115.75</td>
<td>115.09</td>
<td>115.81</td>
<td></td>
</tr>
</tbody>
</table>

As expected, the theoretical spectra calculated for models with different bond distances and angles resulted in electronic states with somewhat different energies and intensities. Since the crystal structures of the other anions did not display identical S-O lengths or OSO angles such a broadening effect is not unlikely. Thus, a distribution of S-O and OSO angles could generate the broad feature observed experimentally. However, the solution spectrum shows the same type of splitting as in the solid state, which would implicate rather large instantaneous deviations from a symmetrical SO$_3$ configuration for the CF$_3$SO$_3^-$ anion also in solution.

4.2.3 Vibrational spectroscopy and normal coordinate analysis

4.2.3.1 Assignment of the vibrational frequencies

Vibrational spectra of the previously studied$^{79,80}$ crystalline CsHSO$_3$ and CsDSO$_3$ compounds were collected. Their fundamental frequencies were assigned based on the potential energy distribution (PED) obtained by means of normal coordinate methods and isotopic shifts (cf. Tables 1, S-2 and S-3, paper VI). The largest frequency shift due to deuteration occurred as expected for the SH/SD symmetric stretching modes. This mode shows very weak coupling with other vibrational modes, as found from the PED. The frequencies calculated for the SH/SD stretchings and bendings deviate slightly from the experimental values, most likely due to anharmonicity, which is not considered in the calculations (Table S-2, paper VI). The assignments are generally in good agreement with those previously proposed.$^{79,80}$

In order to identify the different sulfur(IV) species in aqueous solutions, Raman spectra were measured at room temperature from several 1 M sodium sulfite aqueous solutions at different pH values (pH = 0, pH = 4 both for NaHSO$_3$ and NaDSO$_3$, and pH = 10). The bands were assigned based on the
relative intensity of the bands, isotopic shifts or by comparison to the bands observed for some species in solid state and even literature values. The assignment of the bands is given in Table 2, paper VI. Vibrational frequencies corresponding to hydrated sulfur dioxide molecule and of several anions could be identified: hydrogen sulfite and its deuterated analogue (SO$_3^-$/SO$_3^-$D$^-$), the sulfonate and its deuterated analogue (HSO$_3^-$/DSO$_3^-$) and sulfite (SO$_3^{2-}$). Very weak bands observed at about 430 and 650 cm$^{-1}$ indicate the presence of the disulfite ion (S$_2$O$_5^{2-}$) but in rather small amount.

Vibrational spectra were recorded of crystalline sodium methanesulfonate and sodium trichlate monohydrate and their fundamental frequencies were assigned based on the potential energy distribution achieved by means of normal coordinate analyses (cf. Tables 3, S-4 and S-5, paper VI). The assignment of the bands observed, in particular in the Raman spectrum of the methanesulfonate ion, was complicated due to the splitting and shifting of degenerate modes caused by distortion of the X$_3$CSO$_3^-$ ions from C$_3v$ symmetry or by coupling of the oscillators.

The main change when replacing the hydrogen atoms with chlorine in the methyl group was lowering of the vibrational frequencies, because of the much higher mass of the chlorine atoms. The observed and calculated frequencies together with the PED for the X$_3$CSO$_3^-$ (X=H, Cl, F) anions are included in Table S-5 in Ref. VI. The shift of the C-S stretching to lower frequency for the methanesulfonate, trichlate and triflate ions (793, 620 and 320 cm$^{-1}$, respectively) is partly due to the increasing mass of the CX$_3$ group but also due to the change in the C-S bonding and the coupling with other modes (cf. Tables 3 and S-5). VI Therefore, a comparison of the force constants provides a better measure of the bond strength than the frequencies, see below. The SO$_3$ group vibrations are much less influenced by the substitution of the methyl hydrogen atoms. The SO stretching modes occur in the range 1038 – 1285 cm$^{-1}$, the SO$_3$ bendings at 512 – 637 cm$^{-1}$, and the rocking modes at 341 – 353 cm$^{-1}$. Our assignments for these anions agree fairly well with those reported by Miles et al. and Gejji and coworkers.

4.2.3.2 Force field analysis

The force constants were calculated by the normal coordinate analysis method described in section 2.1.5 for several oxosulfur anions, including also sulfur dioxide and sulfur trioxide (Table 6). The SH stretching force constants calculated for the CsHSO$_3$ compound and the HS radical were found to be similar, 3.80 and 3.89 N cm$^{-1}$, respectively, but are slightly smaller than that calculated for RbHSO$_3$, 3.91 N cm$^{-1}$. The gradual decrease of SH stretching frequencies from 2616 to 2573 cm$^{-1}$ for the solid RbHSO$_3$ and CsHSO$_3$ compounds, respectively, and furthermore to 2535 cm$^{-1}$ observed for this mode in aqueous solution, indicate a weakening of the S-H bond.
The CS stretching force constants calculated for the \( X_3\text{CSO}_3^- \) (\( X = \text{H, Cl, F} \)) ions resulted in the highest force constant for the electron donating methyl group, which increases the C-S bond strength. The smallest value was obtained for the trichlate ion, \( \text{Cl}_3\text{CSO}_3^- \), even though the fluorine atoms of the triflate, \( \text{F}_3\text{CSO}_3^- \), are more electronegative than the chlorine atoms (Table 6). Also the C-X stretching force constants are substantially smaller for the C-Cl bonds. Steric effects because of the increased repulsion between the large \( \text{CCl}_3 \) and \( \text{SO}_3 \) groups seem to be the reason (Fig. 24). This is confirmed by the six Cl \( \cdots \) O contact distances from the crystal structure of the trichlate ion, \( V \), which range from 3.11 to 3.25 Å. The mean value, 3.18 Å, is less than the sum of the non-bonded van der Waals radii, 1.81 Å (Cl) + 1.40 Å (O).\textsuperscript{88}

A plot of the SO stretching force constants and their corresponding S-O bond distances shows an almost linear correlation for the sulfonate ion and its substituted analogues except for the trichlate anion (Fig. 35). The value obtained for sulfonate is larger than that for the methanesulfonate ion, \( \text{H}_3\text{CSO}_3^- \), which implies less \( \pi \)-backdonation from oxygen to sulfur for the methanesulfonate. A Mulliken population analysis (Table 5, paper \textbf{VI}) shows much lower sulfur s electron density but slightly higher oxygen s and p electron population for the hydrated methanesulfonate ion than for sulfonate. The S-O stretching force constant for triflate is higher than that for methanesulfonate, which is consistent with the shorter S-O bond distance in the triflate ion. Even though the S-O bond distance is longer for trichlate than for triflate, the calculated S-O force constant is higher, probably due to the steric repulsion and the weaker S-C bond.

The SO stretching force constants were also evaluated for sulfite and sulfate ions as well as for the sulfur dioxide and trioxide molecules (\textit{cf.} Table 6). The S-O force constants are plotted vs. the S-O bond distances of several oxosulfur species in Fig. 35. In general, the SO stretching force constant increases with decreasing S-O distance (and also increasing OSO angles), except for the trichlate ion, which deviates due to the steric repulsion discussed above. The sulfur dioxide and trioxide molecules with the largest OSO angles and smallest S-O distances have as expected the highest SO force constants.\textsuperscript{VI}
Table 6. Force constants for some oxosulfur species, obtained by normal coordinate analysis.\textsuperscript{VI}

<table>
<thead>
<tr>
<th>Internal coordinates</th>
<th>SO\textsubscript{2}</th>
<th>SO\textsubscript{3}\textsuperscript{2-}</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>SO\textsubscript{3}</th>
<th>HSO\textsubscript{3}\textsuperscript{-}</th>
<th>O\textsubscript{3}SCH\textsubscript{3}\textsuperscript{-}</th>
<th>O\textsubscript{3}SCCl\textsubscript{3}\textsuperscript{-}</th>
<th>O\textsubscript{3}SCF\textsubscript{3}\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textsuperscript{a}Stretch</td>
<td>K(SO)</td>
<td>10.067</td>
<td>5.366</td>
<td>6.592</td>
<td>10.24</td>
<td>7.956</td>
<td>7.601</td>
<td>8.516</td>
</tr>
<tr>
<td>K(CS/HS)</td>
<td>3.800</td>
<td>3.967</td>
<td>2.573</td>
<td>3.492</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(CX); X = H, Cl, F</td>
<td>4.881</td>
<td>2.847</td>
<td>5.758</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{a}Stretch-stretch</td>
<td>f(SO, SO)</td>
<td>0.040</td>
<td>0.690</td>
<td>0.857</td>
<td>0.22</td>
<td>0.164</td>
<td>0.044</td>
<td>0.056</td>
</tr>
<tr>
<td>f(CX,CX)</td>
<td>0.109</td>
<td>0.469</td>
<td>2.607</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>\textsuperscript{b}Bending</td>
<td>H(OSO)</td>
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<td>2.295</td>
<td>2.638</td>
<td>1.321</td>
<td>2.571</td>
<td>1.923</td>
<td>1.804</td>
</tr>
<tr>
<td>H(OSH/OSC)</td>
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<td>1.016</td>
<td>1.060</td>
<td>1.230</td>
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<td></td>
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<tr>
<td>H(XCS)</td>
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<td>1.498</td>
<td>0.691</td>
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<tr>
<td>H(XCX)</td>
<td>0.629</td>
<td>1.601</td>
<td>1.984</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>H(SO\textsubscript{3} out-of-plane bending)</td>
<td></td>
<td></td>
<td></td>
<td>0.632</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>\textsuperscript{b}Bending-bending</td>
<td>h(OSO,OSO)</td>
<td>0.620</td>
<td>0.603</td>
<td>0.362</td>
<td>0.060</td>
<td></td>
<td></td>
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<tr>
<td>h(XCS,XCS)</td>
<td>-0.078</td>
<td>0.223</td>
<td></td>
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<tr>
<td>h(XCX, XCX)</td>
<td>0.044</td>
<td>0.034</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h(OSC,OSC/OSH,OSH)</td>
<td>-0.311</td>
<td>0.495</td>
<td>0.796</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>\textsuperscript{c}Stretch-bend</td>
<td>k(SO,OSO)</td>
<td>0.383</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k(CX, XCX)</td>
<td></td>
<td>0.710</td>
<td>0.460</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>k(CS, XCS)</td>
<td></td>
<td>1.210</td>
<td>-0.387</td>
<td></td>
<td></td>
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<tr>
<td>S-O bond (Å)</td>
<td>1.432</td>
<td>1.505</td>
<td>1.472</td>
<td>1.43</td>
<td>1.441</td>
<td>1.454</td>
<td>1.448</td>
<td>1.433</td>
</tr>
</tbody>
</table>

Force constant units: \textsuperscript{a} 10\textsuperscript{2} N\cdot m\textsuperscript{-1}; \textsuperscript{b} 10\textsuperscript{-18} Nm\cdot rad\textsuperscript{-2}; \textsuperscript{c} 10\textsuperscript{-8} Nm\cdot rad\textsuperscript{-1}. 
4.3 Biologically relevant compounds

4.3.1 XANES spectroscopy and DFT calculations on cysteine, cystine, methionine and methionine sulfoxide

4.3.1.1 Solvated species

The sulfur containing amino acid, cysteine, fulfills various important biological functions in the human body and other organisms due to the ability of its thiol side-chain to undergo redox reactions and also to coordinate heavy metal ions. It usually is accompanied by its oxidized form, the disulfide cystine \( \text{OOC(NH}_3^+\text{)CHCH}_2\text{S-SCH}_2\text{CH(NH}_3^+\text{)COO}^- \)
, as exemplified in recently published analyses by sulfur XANES spectroscopy.\(^5,47,51,111\) Cysteine residues are components in most proteins and the thiol-disulfide ratio has been proposed as a useful indicator of the redox and detoxification status of biological systems such as in blood or in intact cells and tissues.\(^5\)

The cysteine molecule has three ionizable sites, namely the carboxyl, thiol and amino groups. Numerous stability constant determinations have been performed,\(^89-94\) to evaluate the cysteine species present in solution in different pH ranges (\textit{cf.} Fig. 36).\(^\text{VII}\) The protonated cysteine species, \( \text{H}_3\text{Cys}^+ \)
\( ([\text{HSCH}_2\text{CH(NH}_3^+\text{)COOH}]^+) \), dominates for \( \text{pH} < \sim 1 \), while the zwitterion \( \text{H}_2\text{Cys}, \text{HSCH}_2\text{CH(NH}_3^+\text{)COO}^- \)
, which is formed by deprotonation of the carboxyl group, prevails in the range \( 2 < \text{pH} < 8 \). Further \( \text{pH} \)-increase deprotonates both the amonium (\( \text{NH}_3^+ \)) and the thiol (sulphydryl -\( \text{SH} \)) groups almost simultaneously. As a result, two isomeric species coexist in solution, namely the protonated thiol \( \text{HSCH}_2\text{CH(NH}_3\text{)COO}^- \) denoted as \( (\text{HCys})^+ \) in
paper VII and the thiolate, \( \text{`SCH}_2\text{CH(NH}_3^+\text{)COO}^- \) or \((\text{HCys})^-\)''. Above pH \( \approx 10 \) the fully deprotonated form \( \text{Cys}_2^- \), `SCH\(_2\)CH(NH\(_2\))COO\(^-\)' dominates.

\[
\text{[Cys}_2^-\text{]}_\text{TOT} = 50.00 \text{ mM}
\]

**Figure 36.** Fraction diagram showing the major cysteine species at different pH values, calculated for 0.05 M cysteine solution and ionic strength \( I = 0 \text{ M} \) with the macroscopic acidity constants \( pK_{a1} = 10.75 \), \( pK_{a2} = 8.36 \) and \( pK_{a3} = 1.71 \) (Ref. 90).

The sensitivity of the sulfur K-edge XANES spectra to the local environment around the sulfur atom is clearly exemplified for the cysteine system in Fig. 37.\(^\text{VIII} \) The main absorption band observed in the experimental spectra of the solutions up to pH \( \approx 8 \), loses intensity and shifts to lower energy when the thiolate species form.

Methionine, \( \text{CH}_3\text{S(CH}_2\text{)}_2\text{CH(NH}_3^+\text{)COO}^- \), is another sulfur containing amino acid that accomplishes important biochemical functions, however without an ionizable thiol group. It is reversibly oxidized to methionine sulfoxide, \( \text{CH}_3\text{(SO)-(CH}_2\text{)}_2\text{CH(NH}_3^+\text{)COO}^- \).

Since those compounds represent characteristic sulfur functional groups that are often found when evaluating XANES spectra of various biological samples, it is essential to assess their sensitivity to external interactions such as the pH of the medium, hydrogen bonding, etc., to interpret the often overlapping features. For that purpose, theoretical spectra were calculated to assign the experimental spectral features of these biologically relevant compounds to electronic transitions. The effect of hydration on the energy and intensity of the main calculated transitions was examined by connecting several hydrogen bonded water molecules to these species.
Cysteine: pH-dependence. The structural models used for calculations of theoretical spectra for the cysteine species were derived from the crystal structure of L-Cysteine at 120 K, which contained two crystallographically independent conformations for the zwitterionic cysteine.\textsuperscript{95} The L-Cys(A) conformation was selected to describe the thiol species (H\textsubscript{3}Cys\textsuperscript{+}, H\textsubscript{2}Cys and (HCys\textsuperscript{-})\textsuperscript{\prime}), while L-Cys(B) gave spectral features in better agreement for the thiolate species, (HCys\textsuperscript{-})\textsuperscript{\prime\prime} and Cys\textsuperscript{2-}. The hydrogen bonded water molecules added around these species were placed at the following distances: O\textsuperscript{\prime\prime}(H)-O 2.75 Å, N\textsuperscript{\prime\prime}(H)-O 2.8 Å, R\textsubscript{2}S\textsuperscript{\prime\prime}(H)-O 3.5 Å and R-S\textsuperscript{\prime\prime\prime}(H)-O 3.25 Å, with their arrangement illustrated in Fig. 5 of paper VII.
The protonated (H$_3$Cys$^+$) and zwitterionic (H$_2$Cys) cysteine species. The proton removal from the carboxyl group does not cause significant changes on the spectral features of the experimental spectrum, which displays an asymmetric peak at about 2470.6 eV and a broader feature above 2472 eV. The theoretical spectra calculated for the hydrated H$_3$Cys$^+$ and H$_2$Cys cysteine species are displayed in Figs. 38A and 38B. The observed asymmetric peak is generated for both species by the two electronic transitions denoted as 1 and 2. The first transition with the highest cross section for both H$_3$Cys$^+$ and H$_2$Cys cysteine species appears at 2470.6 and 2470.5 eV, respectively.

**Figure 38.** Theoretical S K-edge XANES spectra (solid line) of (A) of the hydrated and protonated cysteine H$_3$Cys$^+$ ion and (B) of the hydrated zwitterion H$_2$Cys compared with the experimental XANES spectrum for cysteine in aqueous solution at pH = 0 and 4.9, respectively (dot-dashed line). The vertical bars represent the calculated transition energies and cross-sections, convoluted with FWHM Gaussians of 1.3/1.1 eV below 2470.9/2475.9 eV, linearly increasing to 8 eV FWHM above 2490.9/2495.9 eV, respectively. The unoccupied molecular orbitals corresponding to the marked transitions are described in the text (Figs. S-1 and S-2, paper VII).
The electronic transition 1 for both species is ascribed to excitation of the electron from S(1s) into an antibonding MO dominated by $\sigma^*(S-H)$ character with some contribution from the lone pair on the sulfur atom and $\sigma^*(S-C)$ character. The intensity and the character of the MO corresponding to transition 2 are affected by the deprotonation of the carboxyl group. The splitting between the two transitions 1 and 2 increased from 0.6 to 0.8 eV and their relative intensity ratio, $I(1) : I(2)$, decreased from 2.2 to 1.4. The MO corresponding to the 2nd transition of the hydrated and protonated cysteine cation is more delocalized. It has antibonding $\pi^*$ character for the carboxyl group and antibonding $\sigma^*$ character for the S-C and S-H bonds, while for the cysteine zwitterion the transition takes place into a more localized antibonding MO of $\sigma^*(S-C)$ character. The transition 3 for the $H_3\text{Cys}^+$ form occurs to an antibonding MO dominated by $\sigma^*(S-C)$ character with some $\pi^*$ contribution from the carboxyl group, while the antibonding MO corresponding to transition 3 of the zwitterion has mainly $\sigma^*(O-H)$ character located on one of the water molecules hydrogen bonded to the aminium ($\text{NH}_3^+$) group, and also some $\sigma^*(S-H)$ contribution (cf. Appendix).

**Deprotonated cysteine: HCys⁻.** The HCys⁻ species comprises two isomeric forms that coexist in solution, namely the protonated thiol (HSCH$_2$CH(NH$_2$)COO⁻ = (HCys⁻)´) and the thiolate (SCH$_2$CH(NH$_3^+$)COO⁻ = (HCys⁻)´´) species, respectively. They form almost simultaneously when the aminium ($\text{NH}_3^+$) and the thiol groups of the zwitterion $H_2\text{Cys}$ deprotonate and they dominate together in the pH range from about 8.3 to 10.8. The experimental spectra of the solutions with pH > 8 change significantly; the intensity of the main asymmetric peak observed at lower pH decreases with increasing pH, while the new feature at 2469.4 eV grows (cf. Fig. 37).
Figure 39. Theoretical S K-edge XANES spectra (solid line) of (A) the hydrated HSCH$_2$CH(NH$_2$)COO$^-$ (HCys$^\cdot$) thiol ion and (B) the thiolate ‘SCH$_2$CH(NH$_3^+$)COO$^-$ (HCys$^\cdot\cdot$), compared with the experimental XANES spectrum for cysteine in aqueous solution at pH = 8.1 and 11.3, respectively (dot-dashed line). The vertical bars represent the calculated transition energies and cross-sections, convoluted with FWHM Gaussians of 1.3/1 eV below 2471.8/2469.6 eV, linearly increasing to 8 eV FWHM above 2491.9/2489.6 eV, respectively.

The theoretical spectrum calculated for the thiol (HCys$^\cdot$) resembles that of the zwitterion (cf. Figs. 39A and 38). This observation is strengthened by the similarity of the MO:s corresponding to the states 1, 2 and 3 calculated for the thiol species of the protonated and zwitterion species of cysteine. The oscillator strength of the transitions 1, 2 and 3 changes with regard to the other examined cysteine species (cf. Tables 2, 3 and 4, paper VII), while the new states 4 and 5 of relatively strong intensity appear. The splitting between the transitions 1 and 2 decreases to 0.5 eV and the character of the MO:s corresponding to these transitions is similar, dominated by $\sigma^*(S-H)$ with some contribution from $\sigma^*(S-C)$ and sulfur lone pair. Transition 3 is assigned to S(1s) $\rightarrow\sigma^*(S-C)$ excitation, while for transitions 4 and 5 most of the electron density transfers to MOs localized on the surrounding water molecules with some contribution from $\sigma^*(S-H)$ (see Appendix).

The solution spectra of the reduced form of the tripeptide glutathione, $\gamma$-glutamylcysteinylglycine, which contains a side chain with a thiol group from the cysteine residue, exhibit a pH dependence very similar to that of cysteine, except that the thiol group for glutathione starts to deprotonate at
slightly higher pH (cf. Fig. S-4, paper VII). The similarity of the theoretical spectra calculated for the (HCys)′ thiol and the H₂Cys zwitterion, together with the experimental observations for glutathione, suggests that the appearance of the new feature at 2469.4 eV is associated with the formation of the thiolate anion, (HCys)″. The energy difference between the main absorption peak at low pH, which is replaced by the new feature appearing at high pH, is 1.1 eV for both cysteine and glutathione.

The theoretical spectrum calculated for the thiolate (HCys)″ is displayed in Fig. 39B. The electronic transitions appear at lower energy and have much lower cross section than for the isomeric thiol (HCys)′ (cf. Table 4, paper VII). The most intense transition 1 calculated for the thiolate (HCys)″ appears at 2469.4 eV and the antibonding MO:s corresponding to this state, as well as 2 and 3, are dominated by σ*(S-C) character; and with some of the electron density transferred to the surrounding water molecules (cf. Appendix).

The position of this new experimental peak remains at 2469.4 eV even at higher pH where the fully deprotonated Cys²⁻ species dominates (cf. Table 1, VII). This observation confirms our hypothesis that this new feature originates from the deprotonated thiolate group, without changing much when the aminium group of the thiolate (HCys)″ deprotonates further to the Cys²⁻ ion. The small changes enable the fitting of the experimental spectra of the cysteine solutions at pH 8.1, 9.4 and 10.2 (cf. Fig. 37 e, f and g) with linear combinations of the experimental spectra of the H₂Cys and Cys²⁻ species to estimate the ratios between thiol and thiolate species in those solutions. The fits are satisfactory as illustrated in Fig. 40, and confirm that the spectra of the thiol (HCys)′ and of the zwitterion H₂Cys are similar (Fig. 37c), and also that the thiolate (HCys)″ spectrum must be similar to that of the fully deprotonated Cys²⁻ anion (Fig. 37i).

The fittings showed the following total amounts of thiolate species with increasing pH values: 21% at pH 8.1; 59% at pH 9.4, and 74% at pH 10.2. By estimating the amount of the zwitterion H₂Cys and the cysteine Cys²⁺ ion at the pH values 8.1 and 9.4 the percentage of the thiolate form (HCys)″ can be obtained (21% ad 55%, respectively) and used to evaluate the acidity constant for the acid-base reaction: H₂Cys → (HCys)″ + H⁺. This evaluation gives pKₐ = pH – log([HCys)″]/[ H₂Cys]) = 8.56 ± 0.10 for the thiolate formation from the zwitterion, which means that the thiol (-SH) group is more acidic than the aminium (-NH₃⁺) group in the cysteine zwitterion.
Figure 40. The experimental spectra (black lines) of cysteine solutions at pH = 8.1 (e); 9.4 (f) and 10.2 (g) compared to linear combinations (circles) of two components corresponding to the zwitterionic form (H₂Cys, dot-dashed) and the deprotonated cysteine anion (Cys²⁻, dashed line), representing thiols and thiolates, respectively. The total amount of the thiolate species increases with increasing pH: 21%, 59% and 74%, respectively.

Cysteine anion, Cys²⁻. In strongly alkaline solutions (pH > ~11, cf. Fig. 37) the Cys²⁻ ion with both the thiol and aminium groups deprotonated becomes the dominant form. The spectral feature at 2469.4 eV with rather low intensity, characteristic for the thiolate group, remains at the same position. The theoretical calculations are, however, more troublesome for a highly charged negative ion, because of the need to delocalize the charge distribution and the extended nature of the molecular orbitals for the excited states. Also the conformation of the fully deprotonated Cys²⁻ anion was found to have significant influence on the calculated spectrum, which was evaluated for three models in different conformation. The first two models were derived from the L-Cys(A) and L-Cys(B) conformations of the zwitterion from the structure of L-Cysteine at 120 K.⁹⁵ The third model was obtained after optimization without symmetry restrictions of the ground state structure geometry of the Cys²⁻ ion by means of DFT methods as implemented in the ADF program using triple-ζ basis sets extended with two polarization functions (TZ2P) (cf. Table 7).⁹⁶,⁹⁷ The solvent effect was simulated by means of the Conductor-
like Screening Model (COSMO) method using the dielectric constant of water, $\varepsilon = 78.5$, for the surrounding medium. In the spectrum calculations using StoBe-deMon DFT program, the hydrogen-bonding expected in aqueous solutions was simulated by five, fifteen and twelve water molecules attached to the carboxyl, amino and thiolate groups at the previously described appropriate distances (cf. Fig. 41 and Fig. 5e, paper VII). Thus, a large number of water molecules around this ion was added to account for the hydrogen bonding and solvation effects from the surrounding water molecules in the aqueous solution and to better distribute and stabilize the charge of the doubly negative anion.

All the spectra computed for the different conformations show discrepancy from the observed spectrum, especially regarding the position and shape of the second peak in the calculated spectra, which does not reproduce the experimental feature well. All three theoretical spectra displayed in Fig. 42 were obtained after applying the calculated relaxation effect corresponding to the first state and the relativistic effect as overall energy corrections. An additional empirical shift was also applied to match the position of the first peak in the experimental and theoretical spectra. The theoretical spectra calculated for several modifications of the optimized model of the Cys$^{2-}$ ion showed that some of the low intensity states obtained in the calculations for the unsolvated Cys$^{2-}$ ion disappeared in the hydrated model (Fig. 42C) leading to a better reproduction of the first experimental peak.
Table 7. The bond distances and angles obtained through optimization for the Cys$^{2-}$ anion. The parameters are labelled according to the figure shown in the table.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_1$-C$_2$: 1.82389</td>
<td>S$_1$C$_2$C$_3$: 112.789</td>
</tr>
<tr>
<td>C$_2$-C$_3$: 1.52245</td>
<td>S$_1$C$_2$H$_6$: 110.310</td>
</tr>
<tr>
<td>C$_3$-C$_4$: 1.52024</td>
<td>S$_1$C$_3$H$_6$: 109.202</td>
</tr>
<tr>
<td>C$_4$-O$_5$: 1.26242</td>
<td>C$_2$C$_3$C$_4$: 107.644</td>
</tr>
<tr>
<td>C$_4$-O$_6$: 1.26255</td>
<td>C$_3$C$_4$N$_7$: 110.851</td>
</tr>
<tr>
<td>C$_3$-N$_7$: 1.44488</td>
<td>H$_6$C$_2$H$_9$: 107.870</td>
</tr>
<tr>
<td>C$_2$-H$_8$: 1.10338</td>
<td>H$_{11}$N$<em>7$H$</em>{12}$: 107.230</td>
</tr>
<tr>
<td>C$_2$-H$_9$: 1.10705</td>
<td>C$_6$O$_5$O$_6$: 125.643</td>
</tr>
<tr>
<td>C$<em>3$-H$</em>{10}$: 1.10644</td>
<td>C$_5$C$_6$O$_5$: 116.893</td>
</tr>
<tr>
<td>N$<em>7$-H$</em>{11}$: 1.03291</td>
<td>C$_3$C$_4$O$_6$: 117.410</td>
</tr>
<tr>
<td>N$<em>7$-H$</em>{12}$: 1.03779</td>
<td>C$_3$N$<em>7$H$</em>{11}$: 105.707</td>
</tr>
<tr>
<td></td>
<td>C$_3$N$<em>7$H$</em>{12}$: 106.257</td>
</tr>
</tbody>
</table>

The first composite experimental peak at 2469.4 eV is fairly well reproduced by the theoretical spectra for all three conformations. It corresponds to several transitions with the most intense ones labeled in Fig. 42; all are attributed to $S(1s) \rightarrow \sigma^*(S-C)$ electronic excitations. Thus, for all three conformations the receiving MOs are of similar character involving the same atoms and also show some charge transfer to the surrounding water molecules (cf. Appendix).

However, none of the models employed could reproduce the broad plateau observed after the narrow spectral feature at 2469.4 eV. The theoretical spectrum calculated for the model corresponding to conformation L-Cys(B) seems to give the closest resemblance with the experimental spectrum (cf. Fig. 42 B). Yet our models fail to reproduce the whole spectrum, which probably is an effect of the incomplete description of the charge distribution, especially around the thiolate group. Note that also the conformation of the Cys$^{2-}$ anion has significant influence on the calculated transition energies and intensities.
Figure 42. Theoretical S K-edge XANES spectrum (solid line) of the deprotonated hydrated Cys$^{2-}$ ion for (A) L-Cys(A) conformation with five hydrogen bonded water molecules, (B) L-Cys(B) conformation with fifteen hydrogen bonded water molecules and (C) optimized conformation of this ion with twelve hydrogen bonded water molecules, compared with the experimental XANES spectrum for cysteine in aqueous solution at pH = 13 (dot-dashed line). The vertical bars represent the calculated transition energies and cross-sections, convoluted with 0.9 eV FWHM Gaussians below 2469.4 eV, linearly increasing to 8 eV FWHM at and above 2489.4 eV.

Cystine. The experimental spectrum of the cystine disulfide molecule in aqueous solution displays two resolved peaks at 2469.85 and 2471.48 eV. For cystine in the solid state the corresponding peaks are found at 2469.95 and 2471.8 eV, i.e. the separation has increased between the experimental peak positions from ca 1.63 eV in solution to 1.85 eV for the solid. VII The
transitions within the second experimental peak, especially the hydrogen bond interactions with the amino group, make its peak position sensitive to changes in the surrounding. No hydration interaction is expected with the disulfide bond as it often is found as the nucleus of a hydrophobic core of the folded protein.

The conformation of the structural model for the zwitterionic form of cystine was derived from the crystal structure of L-cystine at 110 K. The theoretical spectrum simulated for the cysteine species hydrated by eight hydrogen bonded water molecules is displayed in Fig. 43. The most intense transition 1 at 2469.9 eV is to an antibonding MO with $\sigma^*(S-S)$ character. The 2nd experimental peak is composed of the transitions 2, 3 and 4; where the MO corresponding to state 2 is dominated by $\sigma^*(O-H)$ character from one of the water molecules hydrogen-bonded to the aminium group, with some minor contribution from antibonding $\sigma^*(S-C)$. The transitions 3 and 4, at 2471.6 and 2472.0 eV, respectively, are both mainly $S(1s) \rightarrow \sigma^*(S-C)$ excitations, but with some charge transfer to one of the hydrogen-bonded water molecules (see Appendix). The previously reported assignments by Hitchcock and coworkers, who attributed the two features of the double peak to $S(1s) \rightarrow \sigma^*(S-S)$ and $S(1s) \rightarrow \sigma^*(S-C)$ transitions based on comparisons with experimental spectra of the solid dimethyl sulfide and dimethyl disulfide molecules, are in qualitative agreement.

![Figure 43](image)

**Figure 43.** Theoretical S K-edge XANES spectrum (solid line) of the solvated zwitterionic form of the disulfide cystine compared with the experimental XANES spectrum of cystine in saturated aqueous solution at pH = 7.1 (dot-dashed line). The vertical bars represent the calculated transition energies and cross-sections, which are convoluted with 1.1 eV FWHM Gaussians below 2475.2 eV, linearly increasing to 8 eV FWHM above 2495.2 eV.
**Methionine.** The experimental XANES spectrum of methionine in solution is similar to that of the zwitterion of cysteine displaying one asymmetric peak at 2470.76 eV with a shoulder at about 2471.75 eV (Fig. 44). However, the main absorption band observed for methionine is found at 0.2 eV higher energy than that for cysteine. A similar shift toward higher energy was reported previously between the main experimental peaks of the thioether dimethyl sulfide (CH₃SCH₃) and methanethiol (CH₃SH).

Theoretical spectra of the methionine zwitterion calculated for two differently hydrated species with five and six hydrogen bonded water molecules, are shown in Figs. 44A and 44B. The electronic transitions and intensities computed for the former model, without the water molecule hydrogen bonded to the sulfur atom, are significantly different than the ones calculated for the latter (Figs. 44A and 44B). However, a close look at the unoccupied molecular orbitals corresponding to the transitions denoted in their calculated spectra shows that their character remains virtually unchanged. Both calculated spectra reproduce reasonably well the main spectral features; the transitions 1 and 3 at 2470.9 and 2471.5 eV, respectively, occur into MO:s with σ*(S-C) character, with the methyl carbon dominating and with contribution from the methylene carbon. The MO corresponding to state 2, which together with 3 describes the experimental shoulder, has also σ*(S-C) character, now with the methylene group dominating, while state 4 that appears only for the largest model is ascribed to excitation from S(1s) into an MO with lone pair character on the sulfur atom (**cf.** Appendix).
Figure 44. Theoretical S K-edge XANES spectrum (solid line) of the solvated zwitterionic form of methionine with six (A) and five (B) hydrogen bonded water molecules, respectively, compared with the experimental XANES spectrum of 0.05 M methionine in aqueous solution at pH = 7.1 (dot-dashed line). The vertical bars represent the calculated transition energies and cross-sections of methionine solvated with six and five (no water at S) hydrogen bonding water molecules, convoluted with FWHM Gaussians of 1.4/1.5 eV below 2475.2/2474.7 eV, linearly increasing to 8 eV FWHM above 2495.2/2494.7 eV, respectively.

Pickering and coworkers\(^2\) reported that the sulfur K-edge XANES spectra of the similar cysteine and methionine in solution are noticeably different. They obtained two transitions by deconvoluting the main absorption feature, which were tentatively ascribed to S(1s) \(\rightarrow\) \(\sigma^*(S-C)\) and S(1s) \(\rightarrow\) \(\pi^*(CH_2)\) transitions, respectively. Our theoretical calculations for the hydrated molecules show that the main asymmetric peak observed for both compounds is composed of three transitions (cf. Figs. 38B and 44). For cysteine the transitions 1 and 2 dominate, while for the model with a hydrogen bonded water molecule to the thioether sulfur atom of methionine also transition 3 at the same energy as 2 contributes. The splitting (0.8/0.6 eV) between the calculated states 1 and 2 for cysteine and methionine, respectively, is slightly different. The shapes of the molecular orbitals corresponding to the first state for these compounds, are similar and dominated by \(\sigma^*(S-H)\) and \(\sigma^*(S-C)\)
character with some sulfur lone pair contribution for cysteine and methionine, respectively (cf. Fig. 45). The molecular orbitals associated with state 2 are similar for both species and can be described as $\sigma^*(S-C)$, while the 3rd transition is dominated by $\sigma^*(O-H)$ to a hydrogen bonded water molecule on the aminium group with some $\sigma^*(S-H)$ contribution for cysteine but mainly $\sigma^*(S-C)$ contribution for methionine. Our calculations show that, in spite of the similar shape of the experimental spectra corresponding to the zwitterions of cysteine and methionine, the main electronic transitions take place into slightly different unoccupied molecular orbitals due to the relatively different molecular and electronic structures of these compounds. Removal of the water molecule hydrogen bonded to the methionine thioether sulfur atom shows the sensitivity of the transitions 2 and 3 to direct interactions affecting the local charge distribution close to the sulfur atom.

![Methionine (6H₂O) and Cysteine (5H₂O) Molecular Models](image)

**Figure 45.** The shape of the unoccupied molecular orbitals corresponding to transitions 1, 2 and 3 (cf. Figs. 38B and 44A) calculated for the hydrated zwitterion forms of cysteine (5 H₂O) and methionine (6 H₂O).

**Methionine sulfoxide.** The broad asymmetric peak with a shoulder, observed at 2473.32 and 2475.15 eV, respectively, in the experimental sulfur XANES spectrum of methionine sulfoxide in aqueous solution, is relatively well described by the theoretical spectrum computed for the methionine sulfoxide molecular model hydrated by six water molecules (cf. Fig. 46). The first three transitions labeled in Fig. 46 contribute to the first experimental peak, while the transitions 4 and 5 reproduce fairly well the experimental shoulder. The first transition 1 at 2473.5 eV is attributed to a
S(1s) → σ*(S-O) electronic excitation, while the MO corresponding to the transition 2 is dominated by antibonding π*(S-O) character with some σ*(S-C) contribution from the two surrounding carbon atoms. The MO corresponding to state 3 looks like that of 2, although with much less charge transferred to the S-O and S-C atoms and with a substantial contribution to one of the water molecules hydrogen-bonded to the aminium (NH₃⁺) group. The last two states, 4 and 5, at 2474.7 and 2475.1 eV occur into MO:s with very similar character which show a mixed contribution of antibonding σ*(S-C) and σ*(S-O) (cf. Appendix).

The energy and intensity of the main transitions calculated for the hydrated methionine sulfoxide and the unsolvated dimethyl sulfoxide molecule are in good agreement and the MO:s corresponding to these transitions for both species have the same character. Therefore, it seems that dimethyl sulfoxide can serve as a good model for the larger methionine sulfoxide molecule, in particular when the unoccupied molecular orbitals corresponding to these transitions do not get contributions from the methionine functional groups (NH₃⁺ and COO⁻).

![Figure 46](http://example.com/figure46.png)

**Figure 46.** Theoretical S K-edge XANES spectrum (solid line) of the hydrated methionine sulfoxide zwitterion compared with the experimental XANES spectrum of 0.05 M methionine sulfoxide in aqueous solution at pH = 7.1 (dot-dashed line). The vertical bars represent the calculated transition energies and cross-sections, convoluted with 1 eV FWHM Gaussians below 2478.4 eV, linearly increasing to 8 eV FWHM at and above 2498.4 eV.

### 4.3.1.2 Solvation effect

The experimental spectral features observed for sulfur species in aqueous solutions are usually slightly broader and with higher intensity than in solids. In most cases, the self-absorption effects in solid particles reduce the intensity, and hydrogen bonding and dipole-dipole interactions in aqueous solutions cause the broadening of the absorption bands. The intensity of a dipole-allowed transition depends on the contribution of sulfur p-character in the
unoccupied molecular orbitals available at the electronic excitation of the sulfur atom and also on the stronger transition dipole for polar bonding, and usually increases with increasing formal oxidation state of the sulfur atom. It is affected by different factors such as the strength of hydrogen bonding or the geometry and covalency of the bonds.\textsuperscript{47}

When comparing the XANES spectrum of cystine in the solid state with that of cystine in solution the experimental peak positions are separated by 1.85 eV for the solid and 1.63 eV for the solution (Fig. S-7, paper VII). However, no reduction in the separation is found when comparing the solid state and solution spectra of the oxidized form of glutathione, with an -S-S-bond between two cysteine residues, for which the amino groups are engaged in amide bonds (Fig. S-3, paper VII). Thus, the hydrogen bonding of the amino groups has a significant effect on the features of the solution spectrum.

In this study, we generally found that transition energies were only slightly affected by the hydrogen-bonded water molecules added to the different examined species to simulate the hydration in aqueous solutions (cf. Tables 2-7, paper VII). However, the transition probabilities of most states often changed significantly because the hydrogen bonding in the vicinity of the sulfur atom attracts electron density and shifts the charge distribution in the molecule. Even though the changes in the transitions often were small when considering the solvating water molecules, the fit to the experimental spectrum generally improved. On the whole, the S(1s) electronic excitations are rather localized and the solvation effects do not affect the electronic structure substantially, as observed from the shapes of their corresponding molecular orbitals whose character remains virtually unchanged in most cases (cf. Figs. S-1, S-2, S-3, S-5, S-6, S-8 and S-9, paper VII).

4.3.1.3 Mercury(II) cysteine complexes in alkaline aqueous solutions

The thiolate affinity for soft xenobiotic metal ions such as mercury(II) is of particular biological importance for cysteine residues in polypeptides (cf. Table 1), e.g. in glutathione and metallothioneins that are low molecular weight proteins with a high cysteine content. The change in mercury(II) coordination and bonding of the dominating Hg\textsuperscript{II}-cysteine complexes existing in alkaline solutions was structurally characterized by a combined EXAFS, \textsuperscript{199}Hg NMR, UV-vis and Raman spectroscopic study.\textsuperscript{IV} Principal Component Analysis revealed the presence of three major components in several ~0.09 mol dm\textsuperscript{-3} mercury(II) alkaline aqueous solutions with different H\textsubscript{2}Cys/Hg\textsuperscript{II} ratios. The relative amount of the major Hg\textsuperscript{II} species existing in these solutions was evaluated by fitting linear combinations of simulated EXAFS functions for the separate complexes to the experimental EXAFS data, aided by \textsuperscript{199}Hg NMR and Raman results. The dominant components found in the examined solutions are all sulfur-bonded mononuclear species, namely, the
linear [Hg(Cys)$_2$]$^{2-}$, trigonal [Hg(Cys)$_3$]$^{4+}$ and also the novel four-coordinated Hg(Cys)$_4$ complexes (cf. Fig. 47). The mean Hg-S bond distances refined by deconvoluting the EXAFS oscillations were found to be 2.35(2), 2.44(2) and 2.52(2) Å, for the [Hg(Cys)$_2$]$^{2-}$, [Hg(Cys)$_3$]$^{4+}$ and Hg(Cys)$_4$ complexes, respectively. The tetrahedrally coordinated Hg(Cys)$_4$ complex was found to dominate in solutions with large excess of the ligand (ratios $H_2$Cys/Hg$^{II} >5$), while from the S-Hg-S symmetric stretching Raman band at 334 cm$^{-1}$ we found detectable concentrations of the linear [Hg(Cys)$_2$]$^{2-}$ complex in solutions with ratios up to $H_2$Cys/Hg$^{II} = 5$. From $^{199}$Hg NMR, the isotopic shift of mercury(II) thiolates in solutions was used as a sensitive indicator of variations in the amount of [Hg(Cys)$_3$]$^{4+}$ and Hg(Cys)$_4$ complexes that are difficult to ascertain from the EXAFS results. The chemical shift for the four-coordinated Hg(Cys)$_4$ species was estimated to –340 ppm.

![Figure 47. The distribution of [Hg(Cys)$_2$]$^{2-}$, [Hg(Cys)$_3$]$^{4+}$ and Hg(Cys)$_4$ complexes, as estimated from EXAFS, Raman and $^{199}$Hg NMR data. Geometry optimized structure of the Hg(Cys)$_4$ complex dominating in alkaline solutions (pH $\approx 11$) in cysteine excess.](image)

### 4.4 Sulfur compounds in marine-archaeological wood samples by XANES, XPS and SEM spectroscopy

In the autumn after the rainy summer of 2000, while being displayed in the Vasa Museum in Stockholm, numerous spots of acidic salt precipitates were detected on the wooden surfaces of the Swedish warship Vasa. The investigations carried out by X-ray powder diffraction on the crystalline salts revealed several sulfate salts as well as elemental sulfur. This prompted a study of the origin of the sulfate salts and the formation of the acid, which seemed to be catalyzed by iron ions and compounds formed at the corrosion of iron object on the Vasa at the seabed, and later also by cor-
rosion products of iron bolts inserted after the salvage. As a result of those studies, sulfur accumulation in archaeological timber was found to be a general conservation concern for wooden historical shipwrecks worldwide. Therefore, detailed information on the type of sulfur compounds, their location in the wood, and their rate of oxidation to form acid, was required to modify the conservation treatments to be more efficient for long-term preservation of these shipwrecks and their artefacts.

The spectroscopic XPS and XAS methods, in particular sulfur K-edge XANES spectroscopy, provided answers to some of those issues. From the fitting of XPS spectra only limited information regarding the various sulfur forms present in a sample can be obtained, when compared to the results from the analysis of XANES spectra. The XPS spectra usually display two main spectral features originating from photoelectrons from the S\textsubscript{2\textpi} level. By curve fitting the reduced and oxidized sulfur amounts can be obtained, with sulfoxide as a minor intermediate (cf. Figs. 4, 5).

However, also the light elements can be assessed by XPS analyses, and useful information can be obtained, e.g. of the ratio between carbon atoms in different surroundings, which can provide information of the ratio of lignin to cellulose in wood samples (Fig. 48).

![Image](image_url)

**Figure 48. (right)** XPS spectra reveal the carbon and oxygen concentrations along an oak wood core from hull timber of the *Mary Rose*. The two C\textsubscript{1\textpi} peaks at 285.0 and 286.5 eV, together with the oxygen content (high C corresponds to low O) can be interpreted as originating mainly from CH\textsubscript{2} (lignin) and C-O (cellulose) groups, respectively. The lignin to cellulose ratio indicated by their relative sizes increases in degraded wood, and the variations indicate that the degradation by erosion bacteria extends throughout the *Mary Rose* timbers. Silicon originates from silicate particles at surfaces and cracks (cf. Figure 4).

For XANES spectroscopy the progress in instrumentation and in the data treatment methods, nowadays not only allow speciation of the different types
of sulfur species present in natural samples but also detailed information about their microscopic distribution. For the inhomogeneous marine-archaeological wood samples, information on the location and accessibility of the accumulated reduced sulfur compounds is essential for devising treatments of the artefacts.\III Therefore, we examined thin (a few \(\mu m\)) wood slices from historical shipwrecks by scanning x-ray absorption microspectroscopy (SXM).\III The unique x-ray microprobe at beamline ID21 of the European Synchrotron Radiation Facility (ESRF) (see http://www.esrf.eu/UsersAndScience/Experiments/Imaging/ID21/) is capable of mapping sulfur species that absorb x-rays of a characteristic energy with a spectral resolution of 0.5 eV over a sample area at high spatial resolution, < 1 \(\mu m\). The SXM instrument operates under low-grade vacuum at the sulfur K-edge energies, around 2.5 keV to avoid the strong air absorption.

Wood slices of a few \(\mu m\) were cut with razor blades perpendicular to the cell walls. Raster scanning of the sample in the focused beam at energies of characteristic sulfur XANES resonances, ca. 2473 and 2483 eV, were performed to map the distribution of reduced and oxidized sulfur species, respectively. A typical SXM image showing the distribution of reduced sulfur in the cell walls is shown in Fig. 49.\III

**Figure 49.** Scanning x-ray spectromicroscopy (SXM) images of freshly salvaged (in 2004) oak wood from the warship *Mary Rose* after 459 years on the seafloor (pixel size: 0.5 \(\mu m\), integration time / pixel: 600 ms). The left image, at 2473 eV, shows two layers of thiols in high concentration (bright color at the top) in the lignin-reinforced walls of a vessel, which is a channel for water flow in oak wood; the dark patches surrounded by cell walls are the lumina. The image to the right at 2483 eV shows the distribution of oxidized forms (mostly sulfate).
The SXM images obtained of oak wood from hull timber at the x-ray energy 2473 eV consistently reveal high concentrations of reduced sulfur species in the lignin-rich parts of the wood structure, especially in the middle lamella between the cell walls. A sample from a piece of oak wood freshly salvaged after 459 years in anoxic conditions on the seabed, could even show for the first time that the lignin reinforcement of the walls of an oak wood vessel consists of a distinct double layer of lignin (Fig. 49). Evidently, the high concentration of organosulfur in lignin-rich parts must originate from specific reactions between the hydrogen sulfide (or HS\(^-\) ions), which forms in anoxic seabed conditions, and active sites in the lignin of the wood.\(^{III}\)

The ESRF microprobe not only allows scanning x-ray images but also focused micro-XANES spectra from sub-micron spots. Such XANES spectra from spots in the image of the distribution of reduced sulfur in Figure 49, reveal a particle of iron sulfide, probably pyrrhotite Fe\(_{1-x}\)S, and also reduced sulfur in the middle lamella between the cell walls in the form of thiols and disulfides. However, the fairly noisy focused micro-XANES spectra do not allow quantitative evaluations of the different sulfur species, as is possible for the unfocused SSRL XANES spectra of higher signal-to-noise ratio.

Scanning electron microscopy (SEM) is a very useful technique for images with high resolution, but for analytical purposes the energy dispersive (EDS) detection of the fluorescent x-rays (EDS) only allows analyses of the distribution of the elements in the samples, not their oxidation states, see Figure 50. For SEM measurements, slices of core samples were sputtered with a thin graphite layer and mounted on sulfur-free tape. A low-grade vacuum is maintained during the measurements. The information is useful for judging if the sulfur distribution on a microscopic scale is primarily in particles of iron-sulfur compounds or in organosulfur compounds bound in lignin-rich parts. Also, the results indicate if iron occurs as oxide or sulfide particles. The particle in Figure 50 has an Fe:S ratio of about 1:2 and is probably a pyrite particle.\(^1\)
The empirically based data analysis of the XANES spectra allows determination of the relative amounts of the characteristic sulfur groups by fitting linear combinations of normalized spectra of different standard model compounds to the experimental XANES spectrum. The amount found for each model sulfur compound through the curve fitting procedure is assumed to be equivalent to the fraction of that sulfur functional group present in the analyzed sample. This presumes conversely that the surrounding of the sulfur functional groups in the standard model compounds and their chemical and physical state is similar to that in the analyzed sample. Initially, such fitting procedures were not performed on the XANES spectra corresponding to the *Vasa* samples and the major peaks observed at 2473 and 2483 eV were assumed to be mainly elemental sulfur (S$_8$) and sulfate (SO$_4^{2-}$), and the other intermediate species observed were not identified.$^{21}$

The DATFIT program implemented within the EXAFSPAK software package$^{22}$ allows determination of the number of components representing characteristic sulfur chemical forms that can be distinguished in the spectrum of a sample. This is achieved by means of the Principal Component Analysis (PCA) method and is usually employed for a series of XANES spectra corresponding to one sample measured at different depths. However, the number of components determined from PCA does not necessarily need to be equal to the number of standard model compounds refined through the

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**Figure 50.** SEM image (JEOL 820 SEM, equipped with a LINK AN10000 EDS microanalysis system) of transverse section through partially degraded marine archaeological wood from the Burgzand Noord (BZN) wreck site 3, in the Waddensea, the Netherlands, with the wreck resting at a depth of 6 to 9 meters at high tide (see www.bacpoles.nl; sampling sites, No. 13). X-ray fluorescence (EDS) showed the ratio 1:2 of iron and sulfur for the particle (probably pyrite FeS$_2$) located on top of the honeycomb-like structure of cell walls.
curve fitting procedure. This is explained by the similarity of the sulfur K-edge XANES spectra for slightly different compounds that show absorption features in the same region. Cysteine and methionine exhibit very similar XANES spectra, displaying one major absorption band which is 0.2 eV lower in energy for the former. Even though their spectra are quite alike, it was found that the fit improved significantly when both components were used simultaneously. An additional test if the standard models selected are appropriate, and to evaluate the quality of the fitting, is to compare the 2nd derivative of the experimental and fitted XANES spectra. The curve fitting procedure performed on core 1a of Mary Rose revealed the presence of three reduced sulfur compounds in the wood; they overlap and contribute to the strongest features observed at 2473 eV (Fig. 51). Thus, this peak is composite, consisting of several overlapping reduced sulfur species that correspond to disulfides (1); thiols (2) and elemental sulfur (3), while the components labeled as 4 and 5 correspond to sulfoxide (4) and sulfate (5). The comparison clearly shows that the dotted fitted spectrum poorly reproduces the experimental feature at 2476 eV due to the sulfoxide contribution. This may be due to a different chemical surrounding around the sulfur group in the model compound than in the sample.

![Figure 51](image)

**Figure 51.** XANES evaluation of the sulfur species by fitting linear combinations of standard spectra to surface sample of core 1a of the *Mary Rose* resulted in: 1-disulfides (R-SS-R'; 31 atom %S); 2-thiols (R-SH; 23%); 3-elemental sulfur (S8; 36%); 4-sulfoxide (R2SO or R(SO)R'; 4%) and 5-sulfate (SO42-; 6%). Note that the energy scale in this figure is calibrated by setting the lowest energy peak of sodium thiosulfate (Na2S2O3·5H2O) to 2472.02 eV. Analysis performed by Farideh Jalilehvand.

However, by introducing in the fitting as model for the disulfides the standard spectrum of cystine in the solid state (13% of the sulfur amount), for
which the second peak is at slightly higher energy than for cystine in solution (32%), a better fit to the sulfoxide peak can be achieved (see Figure 52). This again emphasizes the need for choosing standard compounds in a state as representative as possible to the components in the sample.

**Figure 52.** Fittings (circles) of standard spectra for two models, A and B, with and without solid cystine, respectively, compared to the surface XANES spectrum (0-3 mm) of *Mary Rose* oak core 3 from the hull (solid line). Standard spectra fitted for model A are: Disulfides R-S-S-R 1 (cystine in solution 32%) + 1’ (solid cystine 13%) total 45%, 2: Thiols R-SH (cysteine pH 7) 23%, 3: Elemental sulfur (S₈ in p-xylene) 8%, 4: Methionine sulfoxide 5%, 5: Sulfonate R-SO₃⁻ (sodiummethylsulfonate) 10%, and 6: Sulfate SO₄²⁻ (pH 6) 7%. Model compounds for B: 1: 45%; 2: 22%; 3: 8%; 4: 7%; 5: 11% and 6: 7%. The fit (for A) improves when solid cystine is included, also in the sulfoxide region (around 2476 eV in the figures). Direct comparison of the 2nd derivative of the experimental and model sulfur XANES spectra is often performed to verify that appropriate components (standard spectra) were chosen for the model spectrum. Note that the energy scale in this figure is calibrated by setting the lowest energy peak of sodium thiosulfate (Na₂S₂O₃·5H₂O) to 2472.02 eV. Analyses performed by F. Jalilehvand.
5 Concluding remarks

A main theme in this thesis has been to develop and apply methods of analysis for reliable interpretation of experimental x-ray absorption fine structure (XAFS) spectra, especially when deconvoluting overlapping spectral features. That need arose especially when performing detailed analyses of marine-archaeological wooden samples for which the sulfur K-edge XANES spectra revealed a number of reduced sulfur components, partly occurring in crystalline compounds (e.g. iron(II) sulfides), partly bonded to lignin (thiols, disulfides, sulfoxides etc.) in a wood matrix and partly hydrated or dissolved in the wax-like polyethylene glycol bulking agent in the wood (sulfates and possibly elemental sulfur). Principal Component Analysis has been introduced to find the number of components in the XAFS spectra. In the analyses each component should be represented by an appropriate standard or model spectrum. A linear combination of the standard spectra can be fitted to the experimental spectra. For EXAFS spectra such standard or model spectra can be simulated theoretically by means of the EXAFS equation applied on a structural model and the relative amounts of the species evaluated, as for solutions with a mixture of Hg(II)-cysteine complexes. For deconvoluting XANES spectra experimental standard spectra still must be used; in the present cases spectra were measured from pure compounds containing characteristic sulfur functional groups. A concern is then how much the different surroundings in the actual (natural) sample influence the model spectrum.

By means of theoretical calculations employing the transition potential method in density functional theory (TP-DFT) the main features in sulfur K-edge XANES spectra, corresponding to the x-ray excitation of sulfur 1s electrons, have been simulated. The transition energies and the intensities can be calculated with reasonable accuracy in most cases, which makes it possible to assess the influence of coordination, pH, hydrogen bonding and other chemical interactions on the spectral features of the sulfur compounds. The methods have been tested on several biologically relevant compounds and also for finding the number of and to analyze coexisting sulfur species in aqueous solutions. In general, the calculated main features could reproduce the observed features in the spectra fairly well, except for the sulfite and the fully deprotonated cysteine anions, which have a double negative charge.

Distinctly different XANES spectra were obtained for aqueous sulfite solutions at different pH values, characterizing the different sulfur(IV) species. Thus, the hydrated molecular sulfur dioxide, SO$_2$(aq), was confirmed to be the only detectable sulfur(IV) species at low pH (< 1), while the hydrated sulfite (SO$_3^{2-}$) ion was found to dominate at high pH. At intermediate pH, two isomeric sulfur(IV) species coexist, namely the hydrated hydrogen sulfite (SO$_3$H) and sulfonate (HSO$_3^-$) anions with the hydrogen atom directly...
bonded to oxygen and sulfur atoms, respectively. Two well-resolved peaks, observed for the aqueous sulfite solution at pH = 3.9 and ambient temperature, were deconvoluted by means of the theoretically calculated spectra for these ions. The best agreement between the experimental and calculated spectra of this solution was achieved for the ratio $\text{SO}_3\text{H}^-$ : $\text{HSO}_3^-$ ≈ 0.72 : 0.28. The relative amount of sulfonate was found to increase at increasing temperature, even though the $\text{SO}_3\text{H}^-$ species still dominates. The equilibrium quotient at 298 K, $Q_d = [\text{SO}_3\text{H}^-] : [\text{HSO}_3^-] = 2.6 \pm 0.5$, obtained in this work from the ratio of the two isomers at the total concentration of 0.05 M without ionic medium, is smaller than the previously reported value obtained by means of $^{17}$O NMR, $Q_d = 4.9 \pm 0.1$, at 1.0 m ionic strength.\textsuperscript{VI}

The crystal structures of deuterated cesium sulfonate (CsDSO$_3$) and sodium trichloromethanesulfonate monohydrate (NaCCl$_3$SO$_3$·H$_2$O) were determined from neutron powder and single-crystal x-ray diffraction data at room temperature. The results from the Rietveld refinement confirmed that the DSO$_3^-$ ion has a trigonal pyramidal structure with the S-D distance 1.38(2) Å,\textsuperscript{VI} while the pyramidal SO$_3$ and CCl$_3$ groups in the Cl$_3$C-SO$_3^-$ ion are linked in staggered conformation in $C_3v$ point group symmetry.\textsuperscript{V} These studies provided the bond distances and angles needed for analyzing trends in the bonding in substituted sulfonate anions, $X_3\text{C-SO}_3^-$, $X = \text{H}$, Cl, F, by means of XANES spectra evaluated by theoretical calculations, in this case also complemented by vibrational spectroscopy. The substitution of the sulfonate hydrogen atom with CX$_3$ groups ($X = \text{H}$, Cl and F), affects the absolute position and intensity of the absorption bands observed in the XANES and vibrational spectra. These changes induced by the CX$_3$ groups of different bonding character were interpreted by means of theoretical DFT calculations, whereas normal coordinate methods were applied to assign their vibrational spectra and evaluate the corresponding force constants. For the sulfonate and methanesulfonate anions their nearly identical S-O bond distances, as well as the chemical similarity of the S-H and S-CH$_3$ bonding, resulted in fairly similar XANES spectra. The splitting of the main band observed when substituting the CH$_3$ group with the more electronegative CCl$_3$ and CF$_3$ groups was correlated to larger instantaneous asymmetry in the S-O bond within the –SO$_3$ group. The electron withdrawing effect, especially of the CF$_3$ group in CF$_3$SO$_3^-$ delocalises the S-O π-bonds, lowers the S-O and increases the CS force constants in comparison with those of the CCl$_3$SO$_3^-$ ion; a result from the vibrational study of these anions. The S-O stretching force constants calculated for several oxosulfur species were found to decrease with increasing mean S-O bond distance except for the trichloromethanesulfonate. This trichlate ion obtains the lowest CS and highest SO stretching force constants in the series of substituted sulfonates. The reason for this deviation must be the steric repulsion between the CCl$_3$ and SO$_3$ groups.\textsuperscript{VI}
The main peaks observed in the experimental XANES spectra of the sulfur-containing amino acids cysteine and methionine as well as their oxidized forms, the disulfide cystine and methionine sulfoxide, respectively, were analysed by theoretically computed spectra. Since all these compounds are used as reference models for interpreting spectra of biological system it is essential to assess their sensitivity to external interactions, such as the pH of the medium, hydrogen bonding or complex formation especially with transition metal ions. The spectra simulated for all the hydrated species of these compounds reproduce fairly well the main observed features. When raising the pH of the solution, the carboxyl, thiol and amino groups of the cysteine molecule deprotonate, which is reflected in their experimental XANES spectra. The protonated (H$_3$Cys$^+$) and the fully deprotonated (Cys$^{2-}$) species of cysteine dominate in strongly acidic and alkaline aqueous solutions, respectively, while the zwitterionic form (H$_2$Cys) prevails in the 1 < pH < 8.3 range. Two coexisting isomeric species of cysteine, the thiol HSCH$_2$CH(NH$_2$)COO$^-$ (HCys)$'$ and the thiolate $'$SCH$_2$CH(NH$_3^+$)COO$^-$ (HCys)$''$, dominate in solution in the range 8.3 < pH < 10.8, because the aminium (NH$_3^+$) and the thiol (SH) groups of the cysteine zwitterion HSCH$_2$CH(NH$_3^+$)COO$^-$ start to deprotonate almost simultaneously. The formation of the thiolate species is indicated by the appearance of a new feature at lower energy in the XANES spectra. The relative amount of the thiolate species was evaluated by fitting the experimental spectra measured in this range with linear combinations of the experimental spectra of the H$_2$Cys and Cys$^{2-}$ species and was used to obtain the microscopic acid dissociation constant for the reaction: H$_2$Cys $\rightarrow$ (HCys)$''$ + H$^+$. This evaluation gives pK$_a$ = 8.56 ± 0.10 for the thiolate formation from the zwitterion.\textsuperscript{VII}

The influence of the intermolecular hydrogen bonding interactions on the transition energies and intensities was assessed for most of these species by calculating their spectra with and without hydrogen bonded water molecules. In general, the transition energies were not much affected by the simulated solvation; the character of the corresponding MO:s remained unchanged in most cases because of the localized character of the transitions. On the other hand, the transition probabilities of many states changed significantly because the hydrogen bonding shifts the charge distribution in the molecule. In most cases, the fit to the experimental spectrum improved when considering the hydrogen bonding water molecules. In general, changes in the charge distribution in the molecular species may cause significant differences between solution and solid state XANES spectra. We also found that the model fitting of the sulfoxide peak in XANES spectra of wood samples improved when cystine in the solid state was introduced as an additional disulfide standard, because of its larger separation between the two characteristic disulfide peaks (see Cystine, p. 71). Such an influence on the results of the fittings by using different standard spectra shows that it is important to use
standard compounds in as similar conditions as possible for the modeling to analyze the relative amounts of characteristic functional sulfur groups in natural samples.

Thiolates, including the fully deprotonated cysteine anion (Cys$^{2-}$), form strong complexes with soft metal ions such as mercury(II). The structures and relative amounts of the major [Hg(Cys)$_n$] complexes (with $n = 2$, $3$, $4$) that coexist in several alkaline aqueous solutions with varying $H_2Cys/Hg^{II}$ ratios were determined by combining results from EXAFS, $^{199}Hg$ NMR, UV-vis and Raman measurements. The mean Hg-S bond distances refined from EXAFS data were found to be 2.35(2), 2.44(2) and 2.52(2) Å for the dominant [Hg(Cys)$_2$]$^{2-}$, [Hg(Cys)$_3$]$^{4-}$ and also the novel four-coordinated Hg(Cys)$_4$ species, respectively. The Hg(Cys)$_4$ complex was found to dominate in solutions with large excess of the ligand (ratios Cys/Hg$^{II} > 5$), while the linear [Hg(Cys)$_2$]$^{2-}$ complex still persists in solutions with ratios up to $H_2Cys/Hg^{II} = 5$.

Sulfoxides have been the subject of several of the studies. The dimethyl sulfoxide molecule has been studied free and as a ligand by means of experimental sulfur K-edge XANES spectra, with interpretations aided by theoretical DFT calculations.$^9$ The main asymmetrical peak observed for the uncoordinated DMSO molecule is generated by three transitions and the antibonding MO:s corresponding to these states in order of increasing energy have character of: $\sigma^*(S-O)$ plus sulfur lone-pair, mainly $\pi^*(S-O)$, and $\sigma^*(S-O, S-C)$, respectively. The experimental sulfur K-edge XANES spectrum of the protonated dimethyl sulfoxide molecule, (CH$_3$)$_2$SOH$^+$, which is the dominating species in highly acidic solution, displays two resolved peaks with very similar intensity and a shoulder on the high energy side generated by two transitions; the MO:s corresponding to these states are very similar to those calculated for the uncoordinated DMSO molecule.

The oxygen coordinated hexakis(dimethyl sulfoxide)metal solvates of the Group 13 trivalent metal ions, Al, Ga, In and Tl, and also the trivalent Group 3 ion Sc, exhibit similar experimental XANES spectra and display larger splitting and a different intensity distribution of the features than for the uncoordinated DMSO molecule, with the largest splitting observed for the [Tl(dmso)$_6$]$^{3+}$ solvate.$^1$ The splitting of the main experimental peak in the XANES spectra (decrease in transition energy from S(1s) to the receiving MO) through coordination is induced by the metal-oxygen orbital interactions in the bonds. This splitting was found to increase generally within comparable groups of metal ions when the $K_{S-O}$ value of the coordinated dimethyl sulfoxide ligand decreases. Since the experimentally probed receiving orbital for the XANES transition contains an anti-bonding combination of sulfur and oxygen atomic orbitals, $\sigma^*(S-O)$, such a decrease in transition energy should mean that the energy difference between the antibonding and the bonding combination, $\sigma(S-O)$, i.e. its counterpart in a covalent bond, has
decreased. This signifies a weaker $\sigma$-contribution to the S-O bond, which is compatible with the lower $K_{S-O}$ force constant when the $\pi$-contribution to the bond remains similar.\textsuperscript{VIII}

The series of the solvated lanthanoid(III) ions provides an opportunity to study the effect of a regular decrease in ionic size with increasing atomic number on the coordination of dimethyl sulfoxide ligands with the same type of donor atom. However, the experimental XANES spectra of the octakis(dimethyl sulfoxide)lanthanoid(III) complexes are very similar and display only slightly broader asymmetric absorption peaks than for uncoordinated dimethyl sulfoxide molecules. Theoretical calculations revealed that the small changes observed in the experimental spectra of the $[\text{M(OMe}_2\text{)}_8]^3^+$ complexes are similar to pure electrostatic interactions between the dimethyl sulfoxide ligand and the trivalent lanthanoid ions.\textsuperscript{VIII}

In addition, the M-O bond distances for a series of crystal structures where the coordination number is known are useful indicators for studying the coordination in solution with EXAFS methods. Single-crystal x-ray diffraction results showed that the $[\text{M(OS(CH}_3\text{)}_2\text{)}_8]I_3$ compounds (M = La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Lu) consist of discrete $[\text{M(OS(CH}_3\text{)}_2\text{)}_8]^3^+$ entities and iodide ions. The lighter and larger lanthanum(III), cerium(III) and praseodymium(III) ions crystallize in the orthorhombic space group $Pbca$ (No. 61) with $Z = 8$, while all the remaining investigated lanthanoid(III) ions were described in the monoclinic space group $P2_1/n$ (No. 14) and $Z = 4$. All the trivalent lanthanoid(III) ions coordinate via the oxygen atom eight dimethyl sulfoxide molecules in a distorted square antiprism. In all cases one or more of the dimethyl sulfoxide molecules were disordered by a twist around the M-O bond, and a novel semi-rigid model was introduced to obtain reliable M-O bond distances, describing each disordered dimethyl sulfoxide ligand with two alternative sites. The mean M-O distances decreased gradually from La to Lu consistent with the decreasing ionic radii, in good agreement with the lattice-independent EXAFS results. A comparison of the EXAFS oscillations at the L\textsuperscript{III} and K-edges of these solvated ions in the solid state and in solution revealed almost identical spectra implying the same coordination geometry. Their vibrational spectra were assigned and normal coordinate analyses were performed. The M-O stretching force constants calculated for these solvates increased smoothly with decreasing M-O bond distances, except for a distinct break between the Pr and Nd, occurring at the change in space group symmetry.\textsuperscript{VIII,IX}

To summarize, the development of dedicated synchrotron-based sulfur XANES spectroscopy has opened up numerous fields of investigations of the ubiquitous element sulfur and its compounds, which occur in nature in a large variety of species and oxidation states, from -II in sulfides to +VI in sulfates. Sulfur is essential for living organisms and has vital functions in proteins and enzymes. The natural sulfur cycle has great impact on the envi-
ronment. The investigations of marine-archaeological wood, with the use of scanning x-ray spectromicroscopy that allows detailed images, revealed a new pathway for how reduced sulfur compounds may enter into coal and oil, by reactions with lignin in humic matter in anaerobic marine sediments. Fossil fuels release atmospheric sulfur dioxide which forms sulfites, which oxidize and causes acidification of natural waters. Clearly, sensitive analytical methods are important to follow the many functions and transformations of sulfur species in biochemical reactions and in our environment. The emerging detailed theoretical interpretation through sulfur XANES spectroscopy providing detailed insight into the connection between electronic structure, reactivity and chemical bonding in sulfur compounds will allow further understanding of vital life science processes. A great advantage for such studies, e.g. for metalloenzymes and coordination compounds, is that x-ray absorption spectra can also be achieved for the metal atoms as e.g. for the mercury-cysteine complexes in the current investigation, allowing structural information by EXAFS studies.
6 Vetenskaplig sammanfattning

Synkrotronbaserad spektroskopi kan användas för att undersöka många viktiga biologiska och miljökemiska funktioner av det allmänt förekommande grundämnet svavel. Denna avhandling beskriver hur K-kantens finstruktur för svavelatomens röntgenabsorptionspektrum, s k XANES (X-ray absorption near edge structure), kan tydas och användas för att analysera funktionella svavelgrupper. Teoretiska beräkningar, med s k transition potential density functional theory, används för att utvärdera hur koordination, pH, vätebindningar, osv. inverkar när S(1s) elektronen exciteras. Analyser, som har utförts på reducerade svavelföreningar i historiska skeppsvrak, bl a Vasa i Stockholm och Mary Rose i Portsmouth, U.K., visar att de reaktioner på havsbotten som leder till svavelansamling i form av tioler i träets ligninrika delar, också i den naturliga svavelcykeln kan anrika svavel i fossila bränslen via humusämnen i syrefattiga marina sediment. XANES-spektra för svavels K-kant har med hjälp av teoretiska beräkningar analyserats för flera biokemiska modellföreningar och för vattenlösningar av cystein- och vätesulfit(IV)isomerer i jämvikt. Cysteinderivat i proteiner har viktiga biokemiska avgiftningsfunktioner, och strukturundersökningar av kvicksilver(II)cysteinkomplex i lösning har utförts med spektroskopiska metoder: EXAFS (Extended X-ray Absorption Fine Structure), Raman och $^{199}$Hg NMR-spektroskopi. Genom att kombinera kristallografi med EXAFS, XANES och vibrationsspektroskopi konstaterades att lantanoid(III)joner koordinerar syreatomer från åtta dimetylsulfoxidligander i ett deformerat antiprisma både i fast fas och i lösning. Medelavståndet för M-O bindningarna i kristallstrukturerna med felordnade dimetylsulfoxidligander stämmer väl överens med de som erhålls från de gitterberoende EXAFS resultaten. Skillnader i dimetylsulfoxidligandernas XANES spektra för de sex-koordinerade solvatiserade grupp 13 jonerna, TI(III), In(III), Ga(III) and Al(III), har tolkats med hjälp av teoretiska beräkningar.
ACKNOWLEDGEMENTS

First of all, I would like to express my gratitude to my supervisor, **Magnus Sandström**, for sharing your vast chemistry knowledge, for support, help and guidance during the last 5 and ½ years. Even though before coming to Sweden, I have never thought about doing a PhD and what research actually implies, I don’t regret making this choice. Besides learning a lot of different methods and combining both physics and chemistry fields in our research, I have seen places, which I never thought of, located in different corners of the world. I will always remember the time spent in SSRL, especially the beam-time when we measured for 3 days in a row and we only slept about 8 hours each. For all the things I have learnt and experienced the last 5 and ½ years, I am indebted to you.

I am very grateful to **Lars Pettersson**, who has taught me everything I know when it comes to theoretical calculations. Even though from the beginning, I believed that I would mostly be involved in experimental measurements, Magnus changed his mind and sometimes in April 2002, he introduced me to you. I wrongly thought then that I would just compute the spectrum of sulfur dioxide, but now, 5 years later, I can easily say that I have computed at least 300 XANES spectra. You and Magnus could always suggest a new model when the agreement between the experiment and theory was not satisfactory. Many times I felt, like we are saying in Romanian, that you “were speaking Chinese to me” (☺). You knew for sure what you were saying and even though I understood every single word I had hard time to understand what you meant. Thank you for everything you taught me and for always fixing the problems I have had with the different programs. (I believe that Magnus is not so skeptic anymore about the results provided by the StoBe-deMon program.)

I am also very grateful to my co-supervisor, **Ingmar Persson**, for teaching me about EXAFS and how to use the EXAFSPAK programs.

Another person who has taught me many useful programs is **Farideh Jalilehvand**. Your thesis has been of great help whenever I needed to know something about EXAFS. I really appreciate you for teaching me how to do the EXAFS data treatment in the WINXAS program and the fitting of experimental XANES spectra by the DATFIT program. Thank you for your help, advices and for taking care of me when I was in Canada.

I am also thankful to **Ulrik Gelius** who spent many hours teaching me all the tricks about the XPS measurements and trusted me so much that he allowed me to do the measurements on the ESCA instrument on my own.

**Janos Mink** and **Misha Skripkin** are grateful acknowledged for teaching me about vibrational spectroscopy and for all the help I got with the normal coordinate calculations. Thank you – Misha - for all the help I got every time I needed it and for showing me how to run the IR and Raman instruments.
I would like to thank the former and present members in our own group: Alireza Abbasi, Yvonne Fors, Elena G., Liuba Stepakova, as well as to all my roommates: Helen Blomqvist, Tadahiro Yokosawa and Norihiro Muroyama. In April 2001, when I came to Stockholm University to meet Magnus for the first time, I encounter you – Ali – and you showed me the way to Magnus’ office. I didn’t know then that we would actually become colleagues and that we would spend many hours together teaching each other about different methods. I really appreciate your friendship, thank you for your advices regarding the different life aspects and for all help; I admit that I never felt embarrassed to ask you stupid questions. Yvonne: we spent many hours together in SSRL, ESRF or while doing the SEM measurements. Thank you for company during those hours and for your willingness to teach me Swedish and translate Swedish words.

Lars Eriksson is grateful acknowledged for assistance when I needed to run the diffractometers or do the data analysis. I hope that I did not bother you too much. I promise that it won’t happen again! Jag skojar bara! ☺

I also want to thank to: Kjell Jansson for showing me how to run the SEM instrument; Lars Göthe for always running my samples on the Guinier–Hägg diffractometer; Hans-Erik Ekström and Pelle Jansson for the technical support; Roffe Eriksson and Per-Erik Persson for solving my computer related problems.

AnnBritt Rönnell, Eva Petterson and Hillevi Isaksson are gratefully acknowledged for always being very helpful with all paper work.

I want to thank you all my colleagues and friends here at the department: Osamu Terasaki, Gunnar Svensson, Lars-Johan Norrby, Jozef Kowalewski, Ingeborg Csöregh, Sven Hovmöller, Arnold Maliniak, Dag Noréus, Margareta Sundberg, Xiaodong Zou, Isabel Izqvierdo-Barba, Karin Söderberg, Kristina Lund, Yasuhiro Sakamoto, Juanfang Ruan, Nanjiang Shu, Ali Sharafat, Miia Klingstedt, Sigita Urbonaitė, Kati Leonova, Lei Shi, Johanna Nylén, Sahar Nikkhoo Aski, Leila Ghalebani, Mikaela Gustafsson, Tuping Zhou, Thomas Björling, Keiichi Miyasaka, Kirsten Christensen and Karin Häggbom S. You have all been nice companions during our lunch breaks.

Thank you - Kristina L.- for the encouragements and the help you provided when I needed.

Karin S. – it has been really nice to assist you while doing the labs of the “General Chemistry” course. You are a very good teacher. Tack ska du ha!

Special thanks to Richard Becker who kindly answered all my questions concerning the different aspects related to the doctoral thesis.

All other past and present members at the Physical, Inorganic and Structural Department who have contributed to make these years to a very nice time.
I also want to thank my other friends outside Stockholm University: Bonnie Leung, Vicky Mah, Adam Schell, Daniel Lundberg, Gunnar Almkvist, Matteo Cavalleri, Mikael Leetmaa, Kersti Nilsson.

Jag vill också tacka mina vänner från fotboll, Carro Andersson och Margarita Jägerholm. Vi hade väldigt kul när vi spelade fotboll i IFK Täbys lag, även om vi förlorade rätt mycket.


Joseph Nordgren, Jinghua Guo, Thorsten Schmitt and Kristina Kvashnina are also acknowledged for their support while being exchange student in Uppsala University.

Thank you – Thorsten - for your help in the very beginning of my stay here in Sweden. Rasplata mea pentru tine a fost Florentina. 😊

I am also indebted to my parents, brothers and sisters, for their support and encouragement during these years.

I would like to show my appreciation to my other friends: Mehrdad Khor-sandi, Pawel, Ramona Mateiu, Lenuta Floricel, Aurelian si Lili Bria, Nicusor Timneanu - who helped me in one way or another.

Ett stort tack till: Yvonne, Angelica, Natalie, Jennifer, Kent och Signe. Det är alltid kul att träffa er; ni har alltid varit vänliga mot mig och har accepterat mig i er familj.

Last, but not least, I would like to thank from the bottom of my heart my wonderful husband - Robert - for all your love, support and help I got throughout the years. Without you, my life here in Sweden would have been so much tougher. TE IUBESC!

Emiliana Damian Risberg
Stockholm, 2007-04-23
References

Appendix

MO:s corresponding to the transitions assigned in paper VII

H$_3$Cys$^+$ (5 H$_2$O)

Cysteine (5 H$_2$O)

(HCys$^-$)' species (5 H$_2$O)

(HCys$^-$)'' species (6 H$_2$O)
MO:s corresponding to the transitions calculated for DMSO species (paper II and in the thesis)
MO:s corresponding to the transitions assigned in paper VI