Investigation of charge-transfer processes in modern synthetic bioinorganic copper complexes by steady-state and time-resolved optical spectroscopy

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Abstract

Copper complexes are quite often the focus of current research due to their widespread occurrence in nature. The copper A center serves as an electron transport centre in the adenosine triphosphate (ATP) producing energy metabolism of cells. The copper containing enzyme tyrosinase is part of the melanin production pathways and catalyzes the oxidation of phenols such as tyrosine.[8, 13, 32]

The aim of this work was to characterize modern synthetic copper complexes which mimic their natural counterparts and to understand their structure and their physical (e.g. charge transfer processes) and chemical properties (e.g. oxidation states). To achieve this several optical spectroscopic methods have been used.

Resonant Raman spectroscopy yielded characteristic energy dependent spectra of the complexes. From these results it was possible to identify a vibrational mode which connects to a charge transfer process transferring electron density from the core to the ligand and vice versa. In addition the influence of different solvents and counter ions has been investigated. It was also possible to determine and validate the oxidation state and the geometry of the copper complexes at the B18 beamline at Diamond Light Source.

Using the gathered information about the incident photon energy which triggers the charge transfer process, time-resolved XAFS measurements at the P11 beamline at PETRA III, allowing pumping at the resonance wavelength, using a liquid jet delivery system have been conducted. This confirmed our previous resonance Raman measurements, and furthermore demonstrated that a charge transfer process with changes in the oxidation state of the copper can be triggered.

Furthermore, a setup for measuring time-resolved fluorescence with a time-resolution of 25 ps has been established. With the use of a monochromator it is possible to also analyze the wavelength dependence of the time constants. A pulse picker with integrated frequency doubler allows for using slower repetition rates of 8 MHz and lower compared to the 80 MHz of the Tsunami laser system used and makes it possible to use the frequency doubled wavelength range for slower decay processes. Accompanied with ongoing work on extending the setup for time-resolved Raman measurements, this will allow for understanding the time constants of the involved charge transfer processes.

Inhaltsangabe

Kupfer-Komplexe sind Verbindungen, die sich dank ihres vielfältigen Vorkommens in der Natur großen Interesses in der Wissenschaft erfreuen. Das Kupfer-A-Zentrum z.B. dient als Elektronentransport-Katalysator im Adenosintriphosphat (ATP) produzierenden Energiestoffwechsel der Zellen. Das Kupfer enthaltende Enzym Tyrosinase ist in Tieren sowie im Menschen an der Melaninproduktion beteiligt und katalysiert die Oxidation von Phenolen wie beispielsweise Tyrosin.[8, 13, 32]

Ziel dieser Arbeit war es, moderne Kupfer-Komplexe, die diesen natürlichen Vorbildern nachempfunden sind, zu charakterisieren und ein Verständnis ihres Aufbaus zu entwickeln, sowie die physikalischen (wie z.B. Ladungstransferprozesse) und chemischen Eigenschaften (wie z.B. Oxidationszusände) zu verifizieren.

Um dieses Ziel zu erreichen, wurden verschiedene optische Spektroskopiemethoden zum Einsatz gebracht. Resonanz-Raman-Spektroskopie wurde verwendet, um charakteristische Spektren der Komplexe bei verschiedenen Anregungsenergien zu erhalten. Hierbei konnte eine optische Anregung identifiziert werden, die einen Übergang zwischen den Oxidationszuständen des Kupfers ermöglicht. Des Weiteren wurden die Einflüsse verschiedener Lösungsmittel und Gegenionen untersucht. Außerdem war es durch Messungen an der Diamond Light Source möglich, die Oxidationszustände und die Geometrie der Komplexe zu bestätigen. Es wurde zudem begonnen, die Möglichkeit für zeitaufgelöste Raman-Messungen zu schaffen und erste Testmessungen durchzuführen.

Unter Verwendung der Informationen über die Anregungsenergie, die obigen Ladungstransfer anstößt, wurden zeitaufgelöste XAFS-Messungen an PETRA III, welche eine Anregung der Komplexe bei der Resonanzwellenlänge erlaubt, mit einem Jet-System durchgeführt. Diese bestätigen die Raman-Messungen und zeigen einen Ladungstransfer und einen Übergang zwischen Oxidationszuständen auf.

Zusätzlich wurde im Rahmen dieser Arbeit ein Aufbau zur Messung zeitaufgelöster Fluoreszenz etabliert, der es ermöglicht, den Zerfall des angeregten Zustands mit einer Zeitauflösung von bis zu 25 ps zu bestimmen. Durch Erweiterung des Aufbaus mit einem Monochromator kann das Fluoreszenzspektrum zusätzlich wellenlängenaufgelöst untersucht werden. Ein Pulspicker mit integriertem Frequenzverdoppler für das Tsunami-Lasersystem ermöglicht es, zur Grundwiederholungsrate des Lasers von 80 MHz, auch Raten von 8 MHz oder weniger für langsamere Fluoreszenzzerfälle zu verwenden. Dies erlaubt es, zusätzlich zur fundamentalen Wellenlänge des Lasers, den kompletten frequenzverdoppelten Bereich für längere Zerfälle zugänglich zu machen. Durch eine gleichzeitige Erweiterung des bestehenden Raman-Aufbaus für zeit-aufgelöste Messungen, ebnete dies den Weg hin zu Untersuchungen der am Ladungstransferprozess beteiligten Zeitkonstanten.

Contents

Li	List of Figures iii			
Li	List of Tables v			
1	Intr	oducti	on	1
	1.1	Copper	r Proteins and Molecules with Copper Centers	1
	1.2	Model	Complexes for Type 1 Copper Proteins	2
2	The	ory		4
	2.1	Interac	tion of Light with Matter	4
	2.2	Raman	1 Spectroscopy	5
		2.2.1	Raman Scattering	5
		2.2.2	$Classical \ Description \ . \ . \ . \ . \ . \ . \ . \ . \ . \ $	6
		2.2.3	Quantum-Mechanical Approach	7
		2.2.4	Peak Shapes	9
		2.2.5	Franck-Condon Principle	10
		2.2.6	Raman Activity	10
		2.2.7	Resonance Raman Spectroscopy	12
		2.2.8	Time-Resolved Raman Spectroscopy	12
	2.3	Fluores	scence	14
		2.3.1	Absorption and Emission	14
		2.3.2	Stokes Shift	16
		2.3.3	Lifetime	17
		2.3.4	Quantum Yield	17
		2.3.5	Quenching	17
	2.4	X-Ray	Absorption Spectroscopy	21
		2.4.1	X-Ray Absorption	21
		2.4.2	EXAFS	23
		2.4.3	XANES	23
3	Exp	erimer	ntal Techniques and Methods	25
	3.1	Resona	ant Raman Spectroscopy	25
		3.1.1	Sample Preparation	25
		3.1.2	Experimental Setup	25
		3.1.3	Calibration	27

		3.1.4	Time-Resolved Raman Spectroscopy	28
	3.2	Fluore	scence Spectroscopy	30
		3.2.1	Sample Preparation	30
		3.2.2	Types of Fluorescence Measurements	32
		3.2.3	Experimental Setup	33
	3.3	X-Ray	Absorption Spectroscopy	37
		3.3.1	Sample Preparation	37
		3.3.2	Synchrotrons	37
		3.3.3	Experimental Setup	38
4	Res	ults an	d Discussion	42
	4.1	Sample	es	42
	4.2	Ramar	n Spectroscopy	44
		4.2.1	Planning the Measurements	44
		4.2.2	Measurements	45
		Paper	· I Catching an Entatic State - A Pair of Copper Complexes $\ldots \ldots \ldots$	51
	4.3	Time-l	Resolved Spectroscopy	57
		4.3.1	Planning the Measurements	57
		4.3.2	Measurements	58
5	Sun	ımary	and Outlook	73
6	Ack	nowled	lgments	75
\mathbf{A}	Soft	ware		77
	A.1	Mono	Control.py	77
	A.2	Config	file for MonoControl.py	84
	A.3	Fit fur	nction creator	85
	A.4	Powerr	meter.py	92
в	List	of Pu	blications	106
Bi	bliog	raphy		107
Ei	desst	attlich	e Versicherung	114

List of Figures

1.1	Molecular structure of $(TMGqu)_2Cu$ and the entatic state $\ldots \ldots \ldots \ldots$	2
2.1	Scattering processes for Raman scattering	6
2.2	Raman peak shapes	10
2.3	Franck–Condon principle and intensities of the transitions	11
2.4	Polarizability of CO_2	11
2.5	Schematic principle of pump-probe Raman measurements	12
2.6	Bonding and antibonding π orbitals and term diagram of Ethylene $\ldots \ldots \ldots$	14
2.7	Jablonski diagram of the fluorescence process	15
2.8	Schematic drawing of the photoluminescence processes and the decay rates $% \left({{{\bf{x}}_{{\rm{s}}}}} \right)$	16
2.9	Schematic drawing of the Stokes shift	16
2.10	Schematic drawing of all processes contributing to the quantum yield q	17
2.11	Energy diagram for acceptor and donor molecule for Förster Resonance Energy	
	Transfer	18
2.12	Schematic plot of the X-ray absorption coefficient and the XANES and EXAFS	
	energy regions	22
3.1	Photograph of the laser lab at the CFEL, Hamburg	26
3.2	Pump-probe Raman setup	27
3.3	UT-3 setup	28
3.4	Pump-probe Raman setup using one Tsunami laser system	29
3.5	Pump-probe Raman setup using two Tsunami laser systems	30
3.6	Delay line calibration process	31
3.7	Comparison of fluorescence spectra at different concentrations of the sample using	
	different qualities of Acetonitrile.	32
3.8	Steady-state and time-resolved fluorescence spectroscopy	32
3.9	Principle of Time Correlated Single Photon Counting (TCSPC)	34
3.10	TCSPC setup	35
3.11	TCSPC Instrumental Response Function	36
3.12	TCSPC full experiment	36
3.13	PETRA III setup.	37
3.14	Jet setup at PETRA III beamline P11	39
3.15	Glass nozzle setup	39
3.16	Diamond Light Source and sample holder	41

4.1	Structure of the hybrid guanidine-quinoline ligands TMGqu and DMEGqu	43
4.2	Chemical structure of Hexafluorophosphate and Trifluoromethanesulfonate	43
4.3	UV-Vis absorption spectra of the ligands and different oxidation states of the	
	TMGqu copper complex	43
4.4	Molecular structure of $(TMGqu)_2Cu$ and the Cu^I and Cu^{II} oxidation state	44
4.5	Overview of the possible laser wavelengths	45
4.6	Raman spectrum of DCM and MeCN	46
4.7	Raman spectrum of $\mathrm{TMGquCu^{I}} @ 417\mathrm{nm}$ and DFT calculated Raman vibrational	
	modes	46
4.8	Raman spectra of TMGquCu ^I PF ₆ and TMGquCu ^I TfO	47
4.9	Raman spectra of $\mathrm{TMGquCu}^{\mathrm{I}}$ and $\mathrm{TMGquCu}^{\mathrm{II}}$ at two different incident photon	
	energies	48
4.10	Peak intensity resonance plot	49
4.11	UV-Vis absorption spectra of the ligands and complexes with the frequency dou-	
	bled wavelength range	57
4.12	${\rm Cu^{I}}$ to ${\rm Cu^{II}}$ transition by optical excitation using XAFS $\ \ldots \ $	59
4.13	Decay times of the excited $\mathrm{TMGquCu}^{\mathrm{I}}$ state using XAFS at various concentrations	60
4.14	Steady state spectra of the TMG qu ligand, the $\mathrm{Cu^{I}}$ and the $\mathrm{Cu^{II}}$ complex and the	
	TRSPC decay	61
4.15	Fluorescence emission spectra of the TMGqu ligand for different incident photon	
	energies	61
4.16	TMG qu fluorescence emission spectrum at $366\mathrm{nm}$ and $410\mathrm{nm}$ incident photon	
	energy	62
4.17	Fluorescence emission spectra of $\mathrm{TMGquCu^{II}}$ for different incident photon energies	65
4.18	$\rm TMGquCu^{II}$ fluorescence emission spectrum at 366 nm and 410 nm incident photon	
	energy	66
4.19	Fluorescence emission spectra of $\mathrm{TMGquCu}^{\mathrm{I}}$ for different incident photon energies	69
4.20	$\rm TMGquCu^{I}$ fluorescence emission spectrum at 366 nm and 410 nm incident photon	
	energy	70

List of Tables

2.1	Various excitations and their significant term of H_{ER}	8
4.1	Chosen wavelengths for energy dependent Raman measurements	44
4.2	Denominator of equation (4.1) and correction factor for Raman peak intensities.	48
4.3	Changes of important geometric properties of the two TMGqu-complexes when	
	being excited	49
4.4	Chosen incident photon energies for fluorescence and Raman measurements	58
4.5	Transient decay times for different sample concentrations	59
4.6	Fluorescence decay times for the TMGqu ligand for different incident photon en-	
	ergies and different emission wavelengths.	63
4.7	Fluorescence decay times amplitudes for the TMGqu ligand for different incident	
	photon energies and different emission wavelengths	64
4.8	Fluorescence decay times amplitudes for the $\mathrm{TMGquCu^{II}}$ complex for different	
	incident photon energies and different emission wavelengths	66
4.9	Fluorescence decay times for the TMGquCu ^{II} complex for different incident pho-	
	ton energies and different emission wavelengths	68
4.10	Fluorescence decay times amplitudes for the $\mathrm{TMGquCu}^{\mathrm{I}}$ complex for different	
	incident photon energies and different emission wavelengths	70
4.11	Decay time comparisons between time-resolved fluorescence and time-resolved	
	XAFS	71
4.12	Fluorescence decay times for the $\rm TMGquCu^{I}$ complex for different incident photon	
	energies and different emission wavelengths	72

Chapter 1

Introduction

Transition metal chemistry is an established field of research, existing for the last 200 years. In the last 50 years, the chemistry of transition metals has been used to test new models for structure and bonding. They are found in groups 3 to 12 and are called *transition* metals because most of them have properties which transition from metallic elements (groups one and two) into the non-metallic elements of groups 13 to 18. Transition metals include widespread elements like iron, elements used in organic dyes like iridium [50], elements which are used e.g. in resistance thermometers like platinum (Pt100) or elements like technetium which does not occur naturally.[27]

Transition metal compounds differ from ionic compounds and covalent compounds of organic chemistry. They form a coordination complex where a donor, also called ligand, donates both of the electrons necessary for the bond into an empty metal orbital of the acceptor. Depending on the number of ligands involved the geometry can be linear for two-coordination, trigonal planar for three-coordination, tetrahedral or square planar for four-coordination and so on. Furthermore distorted versions of these geometries are possible.^[27]

This work focuses on copper complexes that have received immense interest in current research due to their widespread occurrence in nature. The copper A center serves as electron transport centre in the adenosine triphosphate (ATP) producing energy metabolism of cells. The copper containing enzyme tyrosinase is part of the melanin production pathway and catalyses the oxidation of phenols such as tyrosine.[8, 13, 32]

1.1 Copper Proteins and Molecules with Copper Centers

Copper sites in proteins are classified by their physical (spectroscopic and functional) properties.[74] There are type 1, type 2, type 3, Cu_A , Cu_B and Cu_Z centers. Recently type 0 centers have also been found.[48] The list of currently known types is as follows:

- Type 0: These sites feature distorted tetrahedral geometries and short Cu-O bonds (2.35-2.55 Å). They exhibit weak absorption near 800 nm and a narrow parallel hyperfine splitting in Electron Paramagnetic Resonance (EPR).[48]
- *Type 1*: These copper sites exhibit an intensive absorption band at 600 nm due to a charge transfer from Cu to S. Their appearance is why they are also known as blue copper sites.[73]

They are highly efficient electron transfer agents and show a wide reduction potential scale. [37, 48, 76]

- *Type 2*: These sites do not possess intense absorption bands and their EPR resembles aqueous Cu^{II} ions. They show low reduction potentials combined with Hamiltonian coupled (type 3) dicopper sites.[48, 76]
- *Type 3*: These sites consist of a pair of copper centers, each coordinated by three histidine residues. These proteins exhibit no EPR signal due to strong antiferromagnetic coupling.[51]
- Cu_A : The copper A center consists of two copper atoms coordinated among others by two histidines and two bridging cysteine residues. Copper A centers can be found in cytochrome c oxidase and nitrous-oxide reductase. [8, 13, 76, 75]
- Cu_B : Copper B is coordinated by three histidines and is, as copper A, found in cytochrome c oxidase. One of the histidines is covalently bound to a tyrosinase residue.[41]
- Cu_Z : Copper Z centers can be found in nitrous-oxide reductase and feature a tetranuclear Cu cluster bridged with a μ_4 -sulfide.[18]

1.2 Model Complexes for Type 1 Copper Proteins

The complexes studied in this work are biomimetic model complexes for type 1 copper proteins. The (bis)chelate complexes consist of either a Cu^I or a Cu^{II} core with the hybrid guanidinequinoline ligand TMGqu or DMEGqu where the center-ion is bound to four nitrogen atoms of each two quinoline and two guanidine groups.



Figure 1.1: a) Molecular structure of $(TMGqu)_2 Cu$ and b) Superimposed molecular structures of Cu^{I} : darker with solid bonds, Cu^{II} : lighter with dashed bonds. It can clearly be seen that the two structures are twisted toward each other by about 20 degrees.[35]

The coordination geometry exhibits a distorted tetrahedral for Cu^{I} and is distorted squareplanar for Cu^{II} . Due to the 20 degrees rotation between the two oxidation states the system features an "entatic state" geometry (see figure 1.1(b)). This geometry will be the focus of the following resonance Raman study. The influence of the used solvents dichloromethane (DCM) and acetonitrile (MeCN) as well as the influence of the state of matter on the spectroscopic properties (Raman and XAS spectra as well as fluorescence decay times) of the compounds will be shown. Additionally it will be investigated whether the used counter ions also change any of the spectroscopic properties.

Chapter 2

Theory

To fully understand the optical experimental techniques presented in this thesis, one has to explain the fundamental interaction principles of light and matter. Light can be described as a wave consisting of an electric \vec{E} and magnetic field \vec{H} . In 1873 James Clerk Maxwell published his famous "A Treatise on Electricity and Magnetism" describing the interaction of the magnetic and electric field. It is possible to describe the electromagnetic wave using the assigned vector potential **A** and the scalar potential ϕ .[55]

2.1 Interaction of Light with Matter

When a photon interacts with a sample there are multiple ways this interaction can take place depending on the structure of the sample or the wavelength of the photon:

- refraction: The photon changes its propagation direction due to different propagation speeds inside different transmission mediums.
- absorption: The incident photon is absorbed by the sample transferring its energy to the sample, e.g. increasing vibrations and thus heating the sample.
- fluorescence: The incident photon transfers energy to the sample exciting an energetically higher level which radiatively decays emitting another photon of lower energy than the incident photon.
- Rayleigh scattering: Elastic scattering of the photon by particles much smaller than the wavelength of the photon.
- Raman scattering: Inelastic scattering of the photon at atoms or optical phonons of the sample (typical energy ranges from 10 to $3000 \,\mathrm{cm}^{-1}$)
- Brillouin scattering: Inelastic scattering of the photon at acoustic phonons of the sample (typical energy ranges up to a few cm⁻¹)

This interaction of light and matter can be calculated with the Hamiltonian \mathbf{H} as will be described in section 2.2.3.

2.2 Raman Spectroscopy

The scattering of light by matter was studied by Rayleigh in the end of the 19th century [61] and Einstein in the early 20th century. Both discussed the elastic scattering of photons, without a change of frequency of the scattered photon. With the Compton effect where the scattered photon is in the X-Ray wavelength region, the first scattering effect with a change in frequency has been discovered. In 1923 the Austrian quantum physicist Smekal predicted the inelastic scattering for photons in the visible spectrum. It was Raman and Krishnan that finally discovered the effect 1928 in liquids that we now know as Raman effect.[60] Landsberg and Mandelstam independently found the same effects a few days earlier doing experiments on crystals.[54] The Nobel Prize for Raman provoked some controversies [72] as his co-worker Krishnan was not mentioned and Niels Bohr voted to share the Nobel Prize with the Russian scientists but ultimately Raman alone got it.

In the beginnings of Raman spectroscopy, sunlight with filters was used as a light source until in the 1930s mercury lamps were able to offer some sharp monochromatic lines. Still, taking a Raman spectrum took a few hours as photographic techniques had to be used. In the 1940s double monochromators increased the resolution of the spectra, and by 1946 a catalogue of Raman spectra of 172 pure hydrocarbons had been created. In the 1950s the first resonance Raman spectra were recorded. Due to the fact that the monochromatic light sources were low power and the detector side was only slightly improved using photomultiplier devices, not many measurements could be conducted. This fact led to work on a deeper understanding of molecular vibrations and the theory behind them.[31, 49]

All this changed in the 1960s with the advent of Laser light sources which improved light intensity greatly $(x10^4 - x10^6)$ and reduced the amount of sample necessary. Combined with the charge-coupled device (CCD) detectors invented in 1970, the field of Raman spectroscopy took great leaps forward. Coming from ruby lasers, Ar^+ and Kr^+ ion lasers were widely used for Raman spectroscopy. Nd-YAG lasers with a wavelength of 1064 nm have been employed for measurements where fluorescence posed a problem for Raman scattering. Nowadays tunable Ti-Sapphire lasers with flexible harmonics generation (SHG, THG, FHG) and optical parametric amplifiers are used to have access to a broad range of wavelengths. Raman spectroscopy is commonly used in chemistry for molecule fingerprinting and in solid-state physics, but also in archaeology as a non-destructive analysis method to validate the authenticity of historical documents.[11, 17, 31, 53, 84]

2.2.1 Raman Scattering

Raman scattering, as Rayleigh scattering, is a two photon process. Whereas the energy difference between incident and scattered photon is zero (see figure 2.1) for Rayleigh scattering as it is an elastic process, there are two different cases for Raman scattering where this is not the case. Photons can couple to electric, magnetic or vibronic excitations in the material and transfer energy as a result of creation and annihilation processes. This is differentiated into Stokes and Anti-Stokes processes:

For the Stokes process, the material is in its ground state and is excited to a virtual energy level by the photon. The material then returns to the first excited vibronic energy level instead of the ground state. The scattered photon has a reduced energy compared to the incident photon by the amount of the energy difference between ground state and the first excited vibronic state.

For the Anti-Stokes process the material is already in the first excited vibronic state and is excited to another virtual energy level. Contrary to the Stokes process the material then returns to its ground state. The scattered photon then has a higher energy compared to the incident photon by the amount of the energy difference between ground state and the first excited vibronic state.



Figure 2.1: Different scattering processes for Raman scattering. For Rayleigh scattering the energy difference between incident $(\hbar\omega_i)$ and scattered photon $(\hbar\omega_s)$ is zero as it is an elastic process. For the Stokes process the material is in its ground state and is excited to a virtual energy level by the photon. The material then returns to the first excited vibronic energy level. The resulting scattered photon has a reduced energy compared to the incident photon. For the Anti-Stokes process the material already is in the first excited vibronic state and is excited to another virtual energy level. The material then returns to its ground state. The scattered photon then has a higher energy. Adapted from [11].

In thermodynamic equilibrium, more lower energy levels than higher ones are occupied so that the Stokes process is dominating. Compared to Rayleigh scattering, Raman scattered light has a reduced intensity by a factor of around 10^3 to 10^4 .

The spectrum of the emitted photons is called a Raman spectrum, which is plotted as the energy difference respectively wavelength difference of the scattered photon and the incident photon (which is the laser energy in the following experiments). The energy change is called Raman shift and is defined as follows:

$$\Delta \bar{\nu} = \bar{\nu}_0 - \bar{\nu} = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right) \cdot 10^7 \,\mathrm{cm}^{-1} = -\frac{\Delta \lambda}{\lambda \lambda_0} \cdot 10^7 \,\mathrm{cm}^{-1} \tag{2.1}$$

where $\bar{\nu}_0 = 1/\lambda_0 = \nu \cdot c^{-1} = \omega \cdot (2\pi c)^{-1}$ is the wavenumber of the incident photon and $\bar{\nu}$ the wavenumber of the scattered photon with their respective wavelengths λ_0 and λ .

2.2.2 Classical Description

For the classical description of the Raman effect, one starts with an incident light wave \vec{E} (see equation 2.2) that induces a dipole moment μ (see equation 2.3) in the absorbing medium where α is the polarizability of the molecule.

$$\vec{E} = \vec{E_0} \cos \omega_0 t \tag{2.2}$$

$$\mu = \alpha \vec{E} \tag{2.3}$$

The polarizability is now time dependent (see equation 2.4) and the vibration of the molecule can be described by a harmonic oscillator (see equation 2.5) where q is the normal coordinate.

$$\alpha = \alpha_0 + A \cdot \cos \omega_{vib} t \tag{2.4}$$

$$q(t) = q_0 \cos \omega_{vib} t \tag{2.5}$$

Doing a Taylor expansion of α around q = 0 yields:

$$\alpha(q(t)) = \alpha_0 + \left(\frac{\delta\alpha}{\delta q(t)}\right)_{q=0} q(t) + \dots$$
(2.6)

Inserting equation 2.6 into equation 2.3, the dipole moment can be written as:

$$\mu = \mu(t) = \left(\alpha_0 + \left(\frac{\delta\alpha}{\delta q}\right)_{q=0} q_0 \cos\omega_{vib}t\right) E_0 \cos\omega_0 t \tag{2.7}$$

Using only the first two terms the dipole moment can be written as sum of all three parts (Rayleigh, Stokes and Anti-Stokes).

$$\mu(t) = + \underbrace{\alpha_0 E_0 \cos \omega_0 t}_{Rayleigh} + \underbrace{\frac{1}{2} \left(\frac{\delta \alpha}{\delta q} \right)_{q=0}}_{Stokes} E_0 q_0 \cos((\omega - \omega_{vib})t) + \underbrace{\frac{1}{2} \left(\frac{\delta \alpha}{\delta q} \right)_{q=0}}_{Stokes} E_0 q_0 \cos((\omega + \omega_{vib})t) + \underbrace{\frac{1}{2} \left(\frac{\delta \alpha}{\delta q} \right)_{q=0}}_{Anti-Stokes}$$
(2.8)

One can clearly see that the dipole moment can now be written in a way where Rayleigh scattering, Stokes scattering $(\omega - \omega_{vib})$ and Anti-Stokes scattering $(\omega + \omega_{vib})$ are easily identifiable.[11]

2.2.3 Quantum-Mechanical Approach

The classical approach above is descriptive for the direct coupling between incident photon and scattered phonon and therefore the Stokes and Anti-Stokes scattering but incomplete as indirect coupling is missing. For a detailed description it is necessary to use a quantum mechanical approach.

A scattering medium coupled to a radiation field is described by the following Hamiltonian:

$$H = H + H_R + H_{ER} \tag{2.9}$$

$$=H_0 + H_1 + H_R + H_{ER} (2.10)$$

with the following contributions: H the Hamiltonian of the scattering medium, H_R the Hamiltonian of the radiative field and H_{ER} , the Hamiltonian describing the interaction between the radiative field and the electrons in the scattering medium. H can be divided further into H_0 , the Hamiltonian of the various excitations in the medium and H_1 the interaction between these excitations.[31]

Considering the interaction between electrons and the radiation field and assuming the *j*th electron has the momentum operator p_j and position vector r_j , the radiation field can be included in the electronic Hamiltonian by replacing p_j with the following expression:

$$p_j \to p_j + eA(r_j) \tag{2.11}$$

The resulting Hamiltonian then has the form:

$$H_{ER} = H_{ER}^{'} + H_{ER}^{''} \tag{2.12}$$

$$= \frac{e^2}{2m} \sum_j A(r_j) \cdot A(r_j) + \frac{e}{m} \sum_j A(r_j) \cdot p_j \qquad (2.13)$$

where the result for H'_{ER} is called A^2 term which contributes when the scattering process has the same initial and final band state. Otherwise the contribution is weak. H''_{ER} is called the p-A term which contributes to scattering in second order.[64] The following table will give a short overview for which kind of excitations the two terms become significant.

Scattering excitation	Significant term
Free electrons	A^2
Electronic transition of atoms or molecules	р·А
Molecular or crystal lattice vibrations	р·А
Polaritons	р·А
Magnons in ordered magnetic crystals	$\mathbf{p} \cdot \mathbf{A}$
Conduction electrons in crystals	A^2 , p·A
Plasmons in crystals	A^2 , p·A

Table 2.1: Various excitations and their significant term of H_{ER} .[31]

Resonant Raman scattering happens when the energy of the incident photon equals the energy for a transition from an initial $|i\rangle$ to a final $|f\rangle$ state. The components of the polarization tensor $\alpha_{\rho\sigma}$ for such a transition couple to a transition in the system $|i\rangle$, $|f\rangle \rightarrow |r\rangle$, where $|r\rangle$ is an intermediate state. This can be described by the Kramers-Heisenberg-Dirac equation [46]:

$$(\alpha_{\rho\sigma})_{fi} = \sum_{r(\neq i,f)} \left(\frac{\langle f | P_{\rho} | r \rangle \langle r | P_{\sigma} | i \rangle}{\hbar \omega_{ri} - \hbar \omega_0 - i \Gamma_r} + \frac{\langle f | P_{\sigma} | r \rangle \langle r | P_{\rho} | i \rangle}{\hbar \omega_{rf} - \hbar \omega_0 - i \Gamma_r} \right)$$
(2.14)

where ρ and σ are any of the Cartesian coordinates x,y and z. ω_{ri} and ω_{rf} are the transition frequencies from the initial state to $|r\rangle$ and from there to the final state. For small Raman shifts it can be assumed that $\omega_{ri} \approx \omega_{rf}$ and the polarizability is dominated by the transition $|i\rangle$, $|f\rangle$ $\rightarrow |r\rangle$. The probability for an energy transfer from the ground state $|m, t\rangle$ to an excited state $|n, t\rangle$ is given by

$$P_{mn} = \frac{2\pi t}{\hbar} \delta(E_n - E_m) |\langle n| H_{int} |m\rangle|^2$$
(2.15)

with $H_{int} = H_1 + H_R + H_{ER} = H_{int}(t)$ is the time dependent interaction Hamiltonian. The differential Raman cross section, which has to be differentiable and must not be constant with respect to the initial state, is determined by the polarizability and is proportional to the transfer rate, is given by [11, 59, 64]

$$\frac{d^2\sigma}{d\omega d\Omega} = \frac{2\pi}{\hbar} \alpha(\hbar\omega_0) \sum_{n,m} \frac{\mathrm{e}^{-\beta E_n}}{Z} |\langle n| H_{int} |m\rangle|^2 \delta(E_n - E_m + \hbar\omega_0)$$
(2.16)

where $\beta = (K_{\rm B}T)^{-1}$, Z the partition function, $\hbar\omega_0$ the incident photon energy and $\alpha(\hbar\omega_0)$ a proportionality factor which is only constant for small changes in the incident photon energies (see equation 2.14). When H_{int} is small compared to H_0 and making use of time dependent perturbation theory, Fermi's "Golden Rule" equation 2.16 can be written as the following response function:

$$\frac{d^2\sigma}{d\omega d\Omega} = -\frac{2\pi}{\hbar}\alpha(\hbar\omega_0)2(n(\omega)+1)\Im(R(\omega+i\delta))$$
(2.17)
with $n(\omega) + 1 = (1 - e^{-\beta\hbar\omega})^{-1}$.[11, 64]

2.2.4 Peak Shapes

Understanding the imaginary part of the response function is crucial for understanding the Raman process. A solution involves using the second quantization and the Greens function.[64]

The imaginary part is directly related to the line shape of the Raman spectrum and can be described with a Lorentzian profile for example:

$$\Im(R(\omega + i\delta)) = I_0^2 \frac{2\Gamma}{(\omega^2 - \omega_0^2)^2 + 4\Gamma^2}$$
(2.18)

where I_0 is the maximum intensity of the excited phonon, ω_0 its frequency and Γ the full width at half maximum (FWHM). The width is inversely proportional to the lifetime τ of the excited phonon. The lifetime is mainly limited by the interaction with other phonons in the crystal due to the anharmonic potential of the phonons and thus also temperature dependent.[59] Also the Lorentzian profile describes a discrete excitation of phonons without interaction with an electronic background.[53]

A modified Lorentzian shape has been used in the analysis of the data in this work which excludes elastic scattering for $\omega = 0$ in equation 2.18:

$$f_L(\omega) = I_0 \frac{\omega \cdot \Gamma}{(\omega^2 - \omega_0^2)^2 + \Gamma^2 \cdot \omega^2}$$
(2.19)

Another typical Raman line shape is the Fano profile:

$$f_F(\omega) = I_0 \frac{\left(q + \left(\frac{\omega - \omega_0}{\Gamma}\right)\right)^2}{1 + \left(\frac{\omega - \omega_0}{\Gamma}\right)^2}$$
(2.20)

where q is the Fano parameter which describes the asymmetry of the profile. The Fano profile depends on the coupling between phonons and electrons and the phononic and electronic Raman matrix element. The width Γ is inversely proportional to the quadratic Fano parameter thus by fitting the profile it is possible to gather information about the electron-phonon coupling. For q = 0 the Fano profile has the shape of a negative lorentzian with width Γ (FWHM) centered around $\omega_0.[53]$



Figure 2.2: Raman Peak shapes. a) Lorentzian profile and b) Fano profile for different Fano parameters q. For q = 0 the Fano profile has the shape of a negative lorentzian.

2.2.5 Franck-Condon Principle

The Franck-Condon principle is a rule which describes the intensities of vibronic transitions. Due to different shapes of the orbitals the Morse potential of the excited state is slightly shifted to the right (see figure 2.3(a)). The laser excitation is depicted as blue arrow. The atom is excited from the lowest vibrational level to the second one of the excited state as the wavefunctions of these vibrational levels have the most overlap. To understand the intensities of all possible transitions we need to take a look at the vibronic wavefunctions of the ground electronic state and an excited state. The higher the overlap the higher the resulting transition probability and respectively the intensity (see figure 2.3(b)).[19, 25] Molecules in the excited state quickly relax to the lowest vibrational mode of the excited state $(10^{-13} \text{ s to } 10^{-11} \text{ s})$ and then decay to the ground state while emitting a photon.[42]

2.2.6 Raman Activity

Not all vibrational modes lead to a Raman response. Only if the following condition is true, is the vibrational mode called Raman active:

$$\left(\frac{\delta\alpha}{\delta q}\right)_e \neq 0 \tag{2.21}$$



Figure 2.3: Morse potentials and vibronic levels of ground state and excited state (a). The wavefunctions of the first excited vibronic energy level and the second one of the ground state overlap strongly which increases the likelihood of this transition drastically. The potentials are shifted due to the different shapes of the orbitals. (b) Intensity and thus probability of the transitions between the different vibronic states for emission (fluorescence) and absorption. For gases the spectral lines appear as sharp peaks whereas for solids you find an inhomogeneous broadening of the peaks (dashed lines). Graphics adapted from [50].

where α is the polarizability of the molecule, as mentioned in equation 2.4, q the normal coordinate as in (2.5) and e the equilibrium position. For diatomic molecules this condition is always true but as soon as the molecule gets more complex, there are modes where this is not fulfilled anymore.



Figure 2.4: Polarizablity changes in CO_2 for two vibrational modes. At the equilibrium position only for the stretching mode a) the derivative of α is not 0. Thus the stretching mode is Raman active where the bending mode b) is Raman inactive. Adapted from [11].

As shown in figure 2.4, only the stretching mode of CO_2 is Raman active as the polarizability decreases for shorter bond lengths and increases for longer ones whereas for the bending mode, the changes of the polarizability are symmetrical.

2.2.7 Resonance Raman Spectroscopy

Using multiple incident photon energies to probe a system it is possible to get a resonance profile of the system. The signal intensity amplification can be between 10^3 and 10^6 in some cases.[69] Resonance enhancement of a certain transition occurs when the incident photon energy ω_0 is close to one or more allowed electronic transitions, contrary to normal Raman scattering where only "virtual" states are being excited and the excitation does not interact with excited electronic states. Also the polarizabilities are properties of the ground state for normal Raman scattering.[44]

The theory of resonance Raman scattering is the so called Herzberg–Teller expansion of the Kramers–Heisenberg dispersion equation by Andreas C. Albrecht. [3, 2] He and his collaborators showed that resonant enhancement can originate from different mechanisms like Franck–Condon overlap, the so-called A-term, where ground and excited electronic states overlap (see section 2.2.5 for a detailed explanation of the Franck–Condon principle). The A-term is non-zero when the transition is electronic-dipole allowed, which is the case when the incident photon energy is within the contour of an intense charge transfer (CT) or π - π * type absorption band. Furthermore the vibrational overlap integral must be non-zero. For small displacements only one vibration is enhanced, where for larger displacements multiple vibrational levels in the excited state can be reached leading to overtones and combinations thereof in the spectrum. Only symmetrical modes show A-term contributions. Another possibility is the Herzberg–Teller vibronic coupling, so called B-term, which is very weak compared to the A-term contributions and is only important when the A-term is close to zero. [2, 3, 44, 82]

The empirical Tsuboi rule must also be considered, stating that if a Raman mode is enhanced when the incident photon energy is close to an electronic band then the "equilibrium conformation of a molecule is distorted along the normal coordinate for the Raman band on going from the ground to the excited electronic state" [34]. This is valid for any totally symmetric, asymmetric, and degenerate Raman band. [44]

2.2.8 Time-Resolved Raman Spectroscopy



Figure 2.5: Schematic principle of pump-probe measurements. While for steady state measurements there is only a probe beam on the sample for pump-probe measurements b) the sample is excited by a different beam before the probe beam hits the sample. By changing the time difference between pump and probe beams you can study the temporal behavior induced by the pump beam.

As Raman scattering is an instantaneous process it only probes the sample in its current state (see figure 2.5a). To get detailed information about an excited state or the decay thereof another technique has to be used. In pump-probe Raman spectroscopy the sample is exposed to two different light sources (see figure 2.5b), typically lasers. While the first beam excites the sample

to an excited state, the second beam then probes the sample in this state. For time-resolved studies the timing between those two beams has to be carefully adjusted. This is typically done using an adjustable delay line where one of the beam paths is extended by the amount needed for a certain time delay (e.g. 0.3 mm/ps). This way one can study the decay of the excited state and its temporal evolution in detail. As the wavenumbers of the Raman spectrum of pump and probe differ in a few orders of magnitude depending on the difference in incident photon energies, they usually do not overlap. Still to avoid mistakenly taking into account the signal of the pump beam, the background created by the pump beam without the probe is subtracted from the probe signal.

2.3 Fluorescence

First known observations of fluorescence are dated as early as the 16th century. Nicolás Monardes, a Spanish physician and botanist, wrote in Historia Medicinal (Sevilla, 1565) about his investigations about a blue opalescence of a water infusion made from the wood of a Mexican tree which has been used to treat kidney ailments. Bernardino de Sahagún, a Franciscan missionary, independently described the wood, called Lignum nephriticum (kidney wood), in the Florentine Codex.[1]

Another famous fluorescent substance is tonic water (or to be more specific, the quinine inside of it). It is excited by the UV part of the sunlight and emits a blueish glow. First observations and characterizations of this fluorophore date back to 1845 done by Sir John Frederick William Herschel, an English astronomer and chemist, who also did valuable botanical work.[33]

The first correct explanation, published in 1852, of the relation between absorption and fluorescence was done by G.G. Stokes, who worked with quinine sulfate as Lignum nephriticum was no longer available in Europe and its botanical origin unknown.[1] Building on the work of Herschel, Stokes found that most of the fluorescence is polarized in the reflection plane and frequency-shifted to lower frequency (or respectively to longer wavelengths) thus explaining why it is impossible to excite the same fluorescence again with itself.[79, 80]

First spectrofluorometers were developed in the 1950s for monitoring anti malaria drugs, including quinine. This led the National Institutes of Health to develop the first practical spectrofluorometer.[83] Fluorescence spectroscopy has seen rapid growth in the last decades. It has become an important technique in life sciences such as biophysics or biochemistry where it is mainly used in biotechnology, flow cytometry, medical diagnostics, DNA sequencing, forensics, and genetic analysis.[47] It is furthermore used for quantum efficiency determination of organic dyes for optimization of light emitting diodes.[50] Other use cases are XAFS measurements where the molecular structure is derived from the emitted fluorescence.[23]

2.3.1 Absorption and Emission



Figure 2.6: Bonding (a) π orbitals (HOMO) and antibonding (b) π^* orbitals (LUMO) for Ethylene and (c) optical transition (excitation: green arrow) from the bonding π orbital (HOMO) to the antibonding π^* orbital (LUMO) with energy gap E_q . Adapted from [50]

When exciting molecules, electrons can be lifted to higher energetic levels. One has to differentiate between singlet and triplet states. The differences between those are found in energy and spin:

singlet =
$$\frac{1}{\sqrt{2}}[(\downarrow\uparrow) - (\uparrow\downarrow)]$$
 (2.22)

triplet =
$$\begin{cases} (\uparrow\uparrow) \\ \frac{1}{\sqrt{2}}[(\downarrow\uparrow) + (\uparrow\downarrow)] \\ (\downarrow\downarrow) \end{cases}$$
(2.23)

Electrons can either have spin $+\frac{1}{2}$ or $-\frac{1}{2}$. If there are only paired electrons in a molecule the total spin of the system is S = 0. If the system only consists of one electron $S = \frac{1}{2}$. If there are two unpaired electrons S = 1. Also linked to the total spin is the spin-angular momentum vector, L, which is, according to quantum mechanics, allowed to have 2S + 1 states. This gives one possible combination for singlet and three for triplet states which are shown in equations 2.22 and 2.23. The sum and difference are written like this due to the indistinguishable nature of the two electrons.



Figure 2.7: Jablonski diagram of the fluorescence process. An electron is excited from the ground state to S_1 by an incident photon. The energy then quickly decays non-radiatively to the ground state of S_1 and back to S_0 by emitting the lost energy as a fluorescence photon. Adapted from [50].

The ground state usually is a singlet state and is called S_0 . Energetically higher levels are logically written as S_1 , S_2 , etc. Radicals, metal ions and complexes are exceptions to this rule as they sometimes have unpaired electrons in their ground state, thus being triplet states. To reach a triplet state from the ground state an electron has to flip its spin which is impossible using optical excitation with a laser for example.

A spin change is only possible with spin-orbit coupling e.g. with the presence of a heavy metal ion in the molecule. As spin changes are slow processes compared to decays without spin changes radiative decay from triplet states, which involves intersystem crossing when the electron comes from an excited singlet state, is in the range of 10^{-8} s to 10^{-3} s making it one



Figure 2.8: Schematic drawing of the photoluminescence processes and the decay rates. For fluorescence k_{ISC} is zero as no intersystem crossing is happening. k_r is the radiative decay rate and k_{nr} is the non-radiative decay rate for processes such as heat for example. For phosphorescence spin changes can happen, e.g. with the presence of a heavy metal ion which allows spin-orbit coupling, and therefore k_{ISC} is greater than zero. Adapted from [50].

of the slowest relaxations. [56] Compared to intersystem crossing processes, decays from singlet states usually take nanoseconds or even only picoseconds. The two different processes are also known as phosphorescence (triplet \rightarrow ground state) and fluorescence (singlet \rightarrow ground state).

2.3.2 Stokes Shift

As described in section 2.2.1 matter excited with photons has several ways of relaxing back to the ground state. Except Rayleigh scattering, all processes are associated with energy transfer. Additionally there are non-radiative decay paths such as heat, energy transfer processes to and from the solvent or the matrix.



Figure 2.9: For most materials the absorption happens at a lower wavelength region than the fluorescence emission. This can be explained in that an electron is lifted in a higher vibronic level inside the excited singlet state which decays in a non radiative way to the lowest level. The resulting fluorescence is thus shifted to lower energies, or higher wavelengths. Adapted from [50].

When the photon emitted by the excited system has higher energy than the exciting photon, it is called anti-Stokes shift. There are a few materials such as Yttrium oxysulfide doped with gadolinium oxysulfide which show this behavior. Most systems though exhibit a Stokes-shift where the emitted photon has lower energy or a higher wavelength (red shift). This can be explained in that an electron is usually lifted in a higher vibronic level inside the excited singlet state (see figure 2.7) which decays in a non radiative way to the lowest level which then relaxes back to the ground state by emitting a photon of lower energy.

2.3.3 Lifetime

The fluorescence lifetime can be written as the inverse sum of all possible decays of the respective excited state where k_r is the radiative decay rate and $\sum k_{nr}$ the sum of all non-radiative processes:

$$\tau = \frac{1}{k_r + \sum k_{nr}} \tag{2.24}$$

Depending on the sample and the decay paths the decay usually follows a single exponential or multiple exponential law:

$$I(t) = I_0 \sum_{n} exp(-\frac{t}{\tau})$$
(2.25)

2.3.4 Quantum Yield

The quantum yield q of a fluorescent material is defined as the relationship between emitted photons and absorbed photons or radiative decay and all decay pathways including the nonradiative ones. Thus q describes the emitter's effectiveness of reemitting the energy in a way so that photons are emitted. For fluorescent materials the value of q can vary between 5 - 42% [57]. It is important to note here that the quantum efficiency is strongly dependent on the solvent or matrix the emitter is placed into as quenching effects can strongly reduce q. The relationship between q and the radiative decay k_r and non-radiative decays k_{nr} can be written as follows:

$$q = \frac{k_{\rm r}}{k_{\rm r} + \sum k_{\rm nr}} \tag{2.26}$$

It is also clear that all decay processes inside an emitter can be written as a sum of q and (1-q):



Figure 2.10: Schematic drawing of all processes contributing to the quantum yield q and the remaining processes 1 - q. Adapted from [50].

The processes diminishing the quantum efficiency, (1 - q), can be written by transforming equation 2.26:

$$1 - q = 1 - \frac{k_{\rm r}}{k_{\rm r} + \sum k_{\rm nr}} = \frac{\sum k_{\rm nr}}{k_{\rm r} + \sum k_{\rm nr}}$$
(2.27)

2.3.5 Quenching

Quenching effects subsume all effects which reduce the fluorescence intensity of an emitter. There are multiple quenching mechanisms like energy transfer processes, excited state reactions and static and dynamic quenching:

Energy Transfer Processes

The Förster Resonance Energy Transfer is a dipole-dipole interaction. The energy transfer from the excited donor to the acceptor does not result in fluorescence from the donor molecule but from the acceptor molecule instead. Spectral overlap of the emission spectrum of the fluorescent material and the absorption spectrum of the quencher is needed for this energy transfer to occur.[24]



Figure 2.11: Energy diagram for the Förster Resonance Energy Transfer. The energy transfer from the excited donor to the acceptor does not result in fluorescence from the donor molecule but from the acceptor molecule instead. Adapted from [50].

The efficiency of the transfer is given in equation 2.28 where k_{ET} is the rate of the energy transfer.

$$E = \frac{k_{\rm ET}}{k_{\rm r} + k_{\rm ET} + k_{\rm nr}} \tag{2.28}$$

 $k_{\rm ET}$ is defined as:

$$k_{\rm ET} = \frac{R_0^6 \cdot k_{\rm D}}{r^6} \tag{2.29}$$

where $k_{\rm D}$ is the rate of the radiative decay of the donor, r the distance between donor and acceptor and R_0 the Förster distance. The Förster distance is defined as the distance between donor and acceptor where $k_{\rm ET}$ is exactly 50%. You can see in equation 2.29 that the Förster Resonance Energy Transfer scales with r^{-6} . The average distance of the Förster energy transfer is approximately 10 nm.[50]

Compared to the Förster Resonance Energy Transfer, the *Dexter Energy Transfer* is a short range energy transfer. Instead of dipole-dipole interactions, electrons transfer the energy.[22] Therefore an overlap of the wavefunctions of the orbitals involved of the donor and the acceptor molecule is necessary and the electron involved has to have a probability of presence in both orbitals.[50]

The efficiency of the transfer is given in equation 2.28 where $k_{\rm ET}$ is the rate of the energy transfer.

$$E = \frac{k_{\rm ET}}{k_{\rm r} + k_{\rm ET} + k_{\rm nr}}$$
(2.30)

 $k_{\rm ET}$ is defined as:

$$k_{\rm ET} \propto J \cdot \exp\left(-\frac{2r}{L}\right)$$
 (2.31)

where J is the integral over the two overlapping wavefunctions and L the Van-der-Waalsradius. You can see in equation 2.31 that the Dexter energy transfer scales with e^{-r} .

$$I(t) = I_0 \sum -exp(\frac{t}{\tau}) + y_0$$
(2.32)

For both energy transfer processes the absorption and emission spectra are unchanged.

Excited State Reactions

For excited state reactions the involved molecules form an exciplex. This is a short-lived dimer consisting of the excited donor and the acceptor. If the acceptor and excited donor molecules are made up from two identical molecules, the complex is called an excimer, for excited dimer.[12, 28] The emission energy of the exciplex or excimer is lower than of the fluorophore alone.

Static Quenching

Some fluorophores form a complex in their ground state with another molecule. Depending on the properties of the new complex it has lower fluorescence or even none at all. The complex usually shows a different absorption spectrum than the fluorophore and usually breaks up when the temperature is high enough.[47]

To find the influence of the quencher concentration on the fluorescence intensity we need to take a look at the association constant of the complex formation K_S [47]:

$$K_{S} = \frac{[F-Q]}{[F][Q]}$$
(2.33)

where [F] is the concentration of fluorophore not in complex form, [Q] is the quencher concentration and [F-Q] the complex concentration. When the complex does not show fluorescence then the fraction of the remaining fluorescence is given by (F/F_0) where F_0 is the fluorescence intensity without a quencher and F the fluorescence intensity with the quencher. The total concentration of the fluorophore $[F]_0$ is given by:

$$K_S = [F] + [F - Q] \tag{2.34}$$

using equation 2.33 this yields:

$$K_S = \frac{[F]_0 - [F]}{[F][Q]} \tag{2.35}$$

$$=\frac{[F]_0}{[F][Q]} - \frac{1}{[Q]}$$
(2.36)

A small rearrangement and replacing the concentrations by intensities gives:

$$\frac{F_0}{F} = K_S[Q] + 1 \tag{2.37}$$

and shows a linear behavior of F_0/F on [Q] with the association constant as slope.

Dynamic Quenching

Dynamic quenching is also called collisional quenching. The excited fluorophore collides with another molecule and transfers its energy during the collision. The quenching molecule decays non-radiatively e.g. by emitting heat. This behavior can be described by the Stern-Vollmer-Equation (see equation 2.38) which will be derived here briefly [47]:

$$\frac{F_0}{F} = 1 + k_q \tau_0[Q] = 1 + K_D[Q] \tag{2.38}$$

where τ_0 is the fluorescence lifetime without quenching and k_q is the bimolecular quenching constant. The Stern-Vollmer quenching constant is given by $K_D = k_q \tau_0$.

Quenching plots are usually shown as F_0/F plotted against the concentration of the quencher [Q] because the plots are usually linear. Deviations from linearity are mostly a sign for multiple fluorophores in the sample, with at least one species not accessible to the quencher.

The observed fluorescence intensity is proportional to the concentration of the excited state $[F^*]$. When constantly illuminating the sample $d[F^*]/dt = 0$ is given. For the same conditions without and with quencher this can be written as:

$$\frac{d[F^*]}{dt} = f(t) - \gamma[F^*]_0 = 0$$
(2.39)

$$\frac{d[F^*]}{dt} = f(t) - (\gamma + k_q[Q])[F^*] = 0$$
(2.40)

with f(t) the constant illumination function and $\gamma = 1/\tau_0$ the decay rate of the fluorescence without a quencher. With the quencher equation 2.39 an additional decay rate $k_q[Q]$ has to be added. With continuous excitation the excited state concentration is constant so both equations can be set to zero. Dividing equation 2.40 by equation 2.39 yields the Stern-Vollmer equation:

$$\frac{F_0}{F} = \frac{\gamma + k_q[Q]}{\gamma} = 1 + k_q \tau_0[Q]$$
(2.41)

Looking at the lifetimes with and without quenching clearly shows that the quencher changes the fluorescence lifetime as another decay process depopulates the excited state:

$$\tau_0 = \gamma^{-1} \tag{2.42}$$

$$\tau = (\gamma + k_q[Q])^{-1} \tag{2.43}$$

which leads to

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0[Q] = \frac{F_0}{F} \tag{2.44}$$

In contrast to static quenching, which only decreases fluorescence intensity due to complex formation but does not change the fluorescence lifetime of the fluorophore (only τ_0 will be measured), dynamic quenching changes the lifetime of the fluorophore. Further interpretation of the bimolecular quenching constant can be found in [47].

2.4 X-Ray Absorption Spectroscopy

The discovery of X-rays by Wilhelm Conrad Röntgen in 1885 lead to an explosion of subsequent discoveries. X-rays still are part of state of the art experiments and are used in different fields of application such as physics, chemistry and of course medical imaging.[58]

X-ray absorption spectroscopy (XAS) is a powerful technique for gathering information about the geometrical structure (e.g. bond lengths) and electronic state of a sample. It can be used for condensed-matter systems as well as liquid sample delivery systems such as a jet. [23, 35]

The first known X-ray absorption spectra were recorded in 1913 independently first by Julius Hedwig in Germany and just a short period of time afterwards by Maurice de Broglie in France. In both cases monochromatic X-rays of different energies were exposed onto a photographic plate from which sharp lines could be seen afterwards. Neither scientist immediately understood this phenomenon and it was only due to the determination of Maurice de Broglie that a theory and ultimately the new field of X-ray absorption spectroscopy was established. [58]

With the invention of synchrotrons, the brilliance of the X-ray beam can now be raised to a level where, with newer detectors, better measurements can be conducted and the theory improved to finally being able to explain the fine structure which is present in the spectra.^[67, 78]

2.4.1 X-Ray Absorption

X-ray absorption is measured as a function of the absorption coefficient $\mu(E)$ which in turn is a function of Energy E. The absorption can be described with the Lambert-Beer law:

$$I_t = I_0 e^{-\mu(E)d}$$
(2.45)

where I_t is the transmitted X-ray intensity, with I_0 the original intensity and d the thickness of the sample.

The absorption coefficient depends on the atomic number Z, the atomic mass A, the energy E and the sample density ρ :

$$\mu(E) \approx \frac{\rho Z^4}{AE^3} \tag{2.46}$$

This also explains why for higher energies the absorption decreases. A characteristic XAFS spectrum can be seen in figure 2.12(a).

With increasing incident photon energy, there are specific energy levels where the absorption spectrum has some discontinuities, called absorption edges. In these regions, the X-ray energy is sufficient to excite a core electron to the continuum. This photoelectron is scattered by neighboring atoms on its way through the absorbing molecule. The different edges are labeled K (n=1), L (n=2), M (n=3) depending on the shell from which the electron is excited.

The resulting XAFS spectrum can be divided into two regions: a) the X-ray Absorption Near-Edge Structure (XANES) and b) the Extended X-ray Absorption Fine Structure (EXAFS).[16]

To describe the XAFS spectrum one has to understand the basic physical principles of X-ray absorption. As mentioned before, when a molecule is excited with a X-ray beam, the photon gets absorbed and a photoelectron is ejected from an inner shell to an unoccupied state or to



(a) X-ray absorption

(b) Gaq₃ X-ray absorption spectrum

Figure 2.12: a) Schematic plot of the absorption coefficient as function of the X-ray energy. The decrease in absorption is interrupted by four sharp peaks. This so called absorption edge happens when the energy is exactly the ionization energy of a core electron. Above each edge there are so called wiggles which are the EXAFS region described in section 2.4.2 and b) Exemplary X-ray absorption spectrum. For the copper K edge the edge energy would be around 8980 eV. The XANES region is defined as energy range of 50 eV around the edge and the EXAFS region as up to 800 eV above the edge. Adapted from [23].

continuum. Using the de Broglie relation:

$$\lambda = \frac{h}{p} = \frac{h}{m_e v_e} \tag{2.47}$$

where h is the Planck constant, p the momentum of the photoelectron, m_e the mass of the photoelectron and v_e the velocity of the photoelectron, the photoelectron can also be described as a wave which gets scattered by the surrounding atoms. Assuming the energy of the X-ray gets absorbed completely by one electron, the kinetic energy of the electron can be written as difference between the electron binding energy E_0 and the energy of the X-ray photon:

$$E_{kin} = \frac{p^2}{2m_e} = h\omega - E_0 \tag{2.48}$$

with ω the frequency of the incident X-ray photon.

Absorption only occurs when the incident X-ray photon's energy is exactly the energy required to move one of the core electrons to continuum or when there is a valence level not completely filled with electrons. As soon as the X-ray energy is sufficiently high, there is a sharp rise in the absorption spectrum. The shape of the absorption spectrum in the edge regions is made up of interferences between the outgoing and backscattered waves of the photoelectron.

For lower energies, around 10 eV after the absorption edge, the wavelengths are a lot greater than in the EXAFS region. At very low wavevectors k the free path is increased and thus the XANES region is dominated by multiple scattering.

For higher energies, the photoelectron has lower wavelengths than in the XANES region. It is for this reason that single scattering events dominate the EXAFS region.^[23]

2.4.2 EXAFS

Around 50 eV above the XANES edge, multiple scattering effects can be neglected for nearest neighbor calculations. The EXAFS spectrum, defined as the normalized, oscillatory part above the absorption edge, can be written as:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E)}$$
(2.49)

with $\mu_0(E)$ the smooth background absorption, representing the absorption of an isolated atom without any EXAFS effects, and $\Delta \mu_0(E)$ the measured edge jump in the absorption $\mu(E)$ at the energy E_0 .

Typically the EXAFS spectrum is plotted against the wavevector k of the photoelectron:

$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}} \tag{2.50}$$

As the EXAFS spectrum typically has low intensity it is often weighted with k^2 or k^3 . The classical EXAFS equation introduced by Stern, Sayers and Lytle [67, 78] is defined as:

$$\chi(k) = S_0^2 \sum \frac{N_j e^{-2\sigma_j k^2} e^{-2R_j/\lambda(k)} f_j(k)}{kR_j^2} sin[2kR_j + 2\delta_c + \Phi]$$
(2.51)

with the overall amplitude factor S_0^2 , the number of equivalent scatterers which give the coordination number N_j , the temperature dependent root-mean-square fluctuation in bond length σ_j , the interatomic distances R_j , the photoelectron mean free path $\lambda(k)$, the backscattering amplitude f_j , the central atom partial wave phase shift of the final state δ_c and the phase factor Φ which represents the wavelike nature of the backscattering photoelectron. The overall amplitude factor S_0^2 did not appear in the original formula but was later added by Rehr *et al.* who obtained the final equation from a more-detailed many-body theory which also includes multiplescattering effects.[63] Equation 2.51 is only an approximation and has to be modified for many body theory.[23]

2.4.3 XANES

The XANES region is defined as $\pm 30 \text{ eV}$ around the absorption edge. The lower energy compared to the EXAFS region makes it sensitive to low lying states which in turn are important for the binding of the molecule and the electronic structure. The most important feature of the XANES region is the absorption edge or "white line". The term "white line" is commonly also used to describe the maximum of the main absorption peak. The position of the XANES edge depends on the electronic structure of the molecule and is used to determine the oxidation state of the sample. For higher oxidation states the electric charge is also higher, the core electrons have a higher attraction and thus the edge is shifted to higher X-ray energies.[23]

Another important feature of the XANES region is the so called "pre-edge peak". As the X-ray energy is below the ionization threshold, the prepeak acts as an indicator for empty bound states and it depends also on the coordination symmetry around the absorber atom. [4, 10] Until now there is no comparable theoretical way of describing the XANES region as equation 2.51 does for the EXAFS spectrum and the development of theoretical and computational methods

is still ongoing. Due to the influence of the multiple scattering effects XANES is very sensitive even to small structural changes.[23]

Chapter 3

Experimental Techniques and Methods

Several methods have been used in this work to get a good characterization of the copper samples. Resonance Raman spectroscopy has been used for vibrational and atom-binding informations. XAFS measurements have been conducted for studying the oxidation state and geometrical information. Time-resolved XAFS and time-resolved fluorescence measurements were done for the characterization of the excited states as well as the decay and thus the different pathways the excited state takes on its way back to the ground state. Additionally first preparations for time-resolved Raman measurements have begun.

3.1 Resonant Raman Spectroscopy

3.1.1 Sample Preparation

All measured copper complexes were dissolved in 99,8% Acetonitrile (abcr GmbH, Karlsruhe) to a concentration of 10 mM. Future experiments will be done in Chromasolv Plus Acetonitrile (Sigma-Aldrich Laborchemikalien GmbH, Seelze) to avoid impurities in the solvent.

3.1.2 Experimental Setup

For the resonant Raman experiments, a McPherson Ultimate Triple 3 (UT3) Spectrometer [70] was used in conjunction with a pulsed Ti:Sapphire, Tsunami model HP ps 10 W P (Spectra Physics Lasers Inc., California) which was pumped with a green Millennia Pro Xs 10sJS diode laser (Spectra Physics Lasers Inc., California). The fundamental laser line was used for the 721.1 nm measurements, the frequency doubled 2ω (with a FHG, model GWU2 23-PS, Spectra Physics Lasers Inc., California) was used for the 361.2 nm, 374.8 nm, 417.3 nm measurements, while the frequency tripled 3ω was used for measurements at 259.5 nm and 277.8 nm. The laser power in front of the entrance optics was, depending on the wavelength, between 4.4 mW and 24.5 mW. The experiments were conducted in a clean room with constant temperature $(22.0 \,^\circ\text{C} \pm 0.5 \,^\circ\text{C})$ and humidity $(40\% \pm 3\%)$. All experiments were performed at room temperature.

To check the pulse width of the laser, a small part of the Tsunami fundamental was mirrored out using a glass plate and the reflection was then coupled into an autocorrelator (APE GmbH, Berlin, Germany).



Figure 3.1: Laser lab at the CFEL. In the front: Two Ti-Sapphire laser systems. Behind the breadboard: one krypton gas laser. Possible experiments: (Time-resolved) Raman spectroscopy, Ellipsometry, DLS, time-resolved and steady state fluorescence spectroscopy

For x-axis calibration and optimization of the optical pathway, a silicon substrate was adjusted in the laser focus of the UT3 entrance optics. The beam path was adjusted so that a maximum silicon peak intensity was found. As the wavenumber of the silicon peak is known, this position was used to calibrate the x-axis of the spectra.

For bio-inorganic measurements a Suprasil glass cuvette (Hellma Analytics, Müllheim, Germany) was filled with 3 ml solution of the complex dissolved in MeCN with a concentration of 5 mmol/L. The solution was continuously stirred with a magnetic stirring system. The cuvette position inside the UT3 entrance optics was adjusted with a micrometer screw so that at first the laser focus was on the outside glass reflection of the cuvette then on the inside glass reflection and subsequently 80 µm inside the solution.

Before each measurement the laser power was measured using a LM-1 power meter from Coherent Inc. Afterwards the camera background was subtracted and the spectra were white light corrected using an Ulbricht Kugelsystem (Deutscher Kalibrierdienst, Gigahertz-Optik, Puchheim, Germany). The measurements were normalized to an integration time of 1s and a laser power of 1 mW:

$$I_{norm} = \frac{I_{raw} - I_{BG}}{P \cdot t \cdot I_{WL}} \tag{3.1}$$

where I_{raw} is the uncorrected intensity, I_{BG} the background intensity, P the laser power on the sample, t the integration time, I_{WL} the white light intensity.

All measurements were constant in time and the median of at least three measurements is shown. For comparison with the absorption profiles, the measured intensities were corrected for



Figure 3.2: Setup of Resonant Raman measurements. Adapted from [68].

wavelength dependent absorption. The wavelength dependent absorption was measured using UV-Vis-spectroscopy and the measured intensities were corrected using a correction factor:

$$A_{\rm norm} = \frac{I_0 - I_t}{I_0} = 1 - \exp(-2.3 \cdot \epsilon \cdot c \cdot d)$$
(3.2)

where I_0 is the initial intensity, I_t the transmitted intensity, ϵ the molar absorption coefficient, c the concentration and d the path length of the laser inside the solution.

3.1.3 Calibration

Window Definition

Assuming the optical axis of the instrument has already been defined by two adjustment lasers which enter the spectrometer from the front and from the back side, multiple windows have to be defined for different wavelength regions. This is done by moving the stepper motors inside the monochromators which move the gratings. The windows are evenly spread over the whole sensitivity range of the instrument, overlap at their edges and are fine tuned using white light shape optimization. This is done by moving the position of mono one and two independently.

Frequency Calibration

After the windows are defined the wavelength range of each of the windows has to be determined. For this a neon calibration lamp is put into the focus of the entrance optics. The resulting


Figure 3.3: The UT3 Raman spectrometer setup consists of the entrance optics with a cassegrain type design and is fully achromatic due to the use of reflective optics. Using three monochromators and a relay-stage high stray light rejection and high resolution are achieved. Adapted from [70].

spectrum is then compared to known peak positions and a function (see equation 3.3) for each window is derived by fitting the mapping.

$$f(\text{Pixel}) = m \cdot \text{Pixel} + \lambda_{Offset} \tag{3.3}$$

with m the slope and λ_{Offset} the offset of the fit function.

White Light Calibration

For retrieving the working function of the spectrometer a Ulbricht sphere white light lamp is used and measured for all the windows previously defined. The background (I_{BG}) has to be subtracted and the measured raw white light (I_{WLraw}) then has to be normalized to the spectral intensity of the Ulbricht sphere $(I_{WLcalibrationlamp})$ which is provided by the manufacturer. The calibration spectrum is split using the frequency calibration of the windows and is then used to normalize the raw white light. This yields the actual working function of the spectrometer.

$$I_{\rm WF} = \frac{I_{\rm WLraw} - I_{\rm BG}}{I_{\rm WLcalibrationlamp}}$$
(3.4)

3.1.4 Time-Resolved Raman Spectroscopy

For previous time-resolved Raman measurements [66] the setup from figure 3.4 has been used. Using only one Tsunami laser system limits the incident photon energies as the pump and probe energies are coupled. In [66] the 2ω pump wavelength has been set to 360.4 nm and the probe wavelength to 720.8 nm respectively.

For the newer time-resolved Raman measurements the standard Raman setup (as in figure 3.2) was extended using another set of Millennia and Tsunami laser systems and an additional



Figure 3.4: Setup of time-resolved Raman measurements using only one Tsunami laser systems. The pulse width of the laser is monitored using a small fraction of the fundamental laser line and an autocorrelator (AC). The fundamental laser line and either the frequency doubled or tripled line can be used for pump-probe experiments. Using a delay line in one of the two beams paths, temporal overlap of the pulses on the sample is achieved. Using a beam expander setup on xyz-stages before the entrance optics, a small spot size and spatial overlap can be accomplished. Adapted from [68].

FHG unit. The repetition rate of the second Tsunami laser is adjusted via a Lok-to-Clock system (Model 3930, Spectra Physics Lasers Inc., California) which takes one laser as reference system and sets the repetition rate of the second accordingly. Spatial overlap is achieved using the periscope and aligning the two beam paths (two non overlapping spots can be seen in figure 3.6(a)) using the last lens of both still separate beam paths. This is done until both focal points on the sample overlap.

Afterwards a delay-line (GTS70, Newport, California) with 70 mm travel and its positions and their according time differences has to be calibrated. Therefore a custom-made UPD-30 fast photo diode (ALPHALAS GmbH, Göttingen, Germany) is put into the entrance optics where both pulses are overlapping. The "Time at Maximum" of both pulses is determined using a 20 GHz Oscilloscope (Picoscope model 4312, Pico Technology, St Neots, United Kingdom) so that the position in time of both pulses is known and the difference can be calculated. Moving the pulses closely together is done by changing the cable length of the reference input of the Lok-to-Clock controller and the final fine tuning is done via the delay line. The plot gives a nice line shape. With fitting one can easily determine the zero position at which both pulses overlap. Using the fit you can now set the delay-line to a position where the time-delay between pump and probe beams is the right one for the next measurement.



Figure 3.5: Setup of time-resolved Raman measurements using two Tsunami laser systems. Both lasers are connected with a "lok-to-clock" system (LTC) which synchronizes the repetition rate to one reference laser. The pulse width of both lasers is monitored using a small fraction of the fundamental laser line and an autocorrelator (AC). The fundamental laser line or any of the frequency doubled/tripled lines can be used for pump-probe experiments. Using a delay line in one of the two beams paths, temporal overlap of the pulses on the sample is achieved. Using a beam expander setup on xyz-stages before the entrance optics, a small spot size and spatial overlap can be accomplished. Adapted from [68].

3.2 Fluorescence Spectroscopy

3.2.1 Sample Preparation

The samples were prepared under nitrogen atmosphere in a Braun Box with water and oxygen concentration <0.5 ppm. After preparation they were filled into cuvettes and put in a sealable DURAN glass (DURAN Group GmbH, Germany) for transportation to the optics labs. The cuvettes have been taken out of the glass just before the measurements to avoid oxidation or sample degradation. All measured copper complexes (see chapter 4.1) were dissolved in Chromasolv PlusTM Acetonitrile (Sigma-Aldrich Laborchemikalien GmbH, Seelze) or LCMS grade Acetonitrile (Sigma-Aldrich Laborchemikalien GmbH, Seelze) to avoid impurities in the solvent. Multiple concentrations of the sample were prepared and will be discussed in chapter 4.3.

As for the Raman and the XAFS measurements 10 mM solution was used, effects of the purity of the solvent only play a small role compared to fluorescence measurements that go as low as 1×10^{-6} mM. Effects of impurities which also show fluorescence quickly pose a problem which can be seen clearly in figure 3.7(a) where for concentrations lower than 0.001 mM a shift towards the emission of the solvent, here anhydrous Acetonitrile, can be observed. When using



(a) Spatial overlap on the sample



(b) Delay line with two mirrors



Figure 3.6: Delay line calibration process: a) First the beam path is built with an GTS70 delay line connected to a XPS-Q2 motion controller (not on the image) with two mirrors mounted in a kinetic mirror mount. b) Then both beam paths are aligned so that the two spots on the sample overlap. For illustrational purposes two non overlapping focal points on a copper sample are shown. The image is taken with a periscope inside monochromator #1 and a Coherent beam view analyzer camera. c) Afterwards the delay line calibration is done by putting a fast photo diode in the sample position, moving the delay line and measuring the time delta between the pulses for a given position. After fitting the position where both pulses overlap perfectly can be easily determined.

spectroscopy grade purified solvent as can be seen for Chromasolv PlusTM Acetonitrile in figure 3.7(b), no shifts happen and the fluorescence signal is always the one of the complex. For all shown measurements Chromasolv PlusTM Acetonitrile or LCMS grade Acetonitrile has been used.



Figure 3.7: a) Steady-state measurements of the DMEGqu copper complex in anhydrous acetonitrile. One can clearly see that for lower concentrations the peak is shifted towards the position of solvent peak (scaled by two to show the peak more prominently). This is due to impurities in the solvent. When using a purified solvent like Chromasolv PlusTM in b) no shifts can be seen.

3.2.2 Types of Fluorescence Measurements

Fluorescence measurements were typically performed in one of two modes: steady-state and time-resolved (see figure 3.8).



Figure 3.8: Comparison of a) steady-state and b) time-resolved fluorescence spectroscopy. Figure adapted from [47].

Steady-State Fluorescence

For steady-state measurements, the sample was illuminated with constant laser power and the fluorescence collected for a certain amount of time. Due to the decay times being as fast as micro, nano- or picoseconds these measurements can be regarded as steady-state. The measurements were usually done by using a grating to split a beam into its components and using a detector to register the intensity of each fraction. For the steady-state measurements a Ocean Optics QE65000 Peltier cooled spectrometer was used.

Time-Resolved Fluorescence

The other type of measurement are time-resolved measurements where the sample is excited with a laser pulse that has to be shorter than the lifetime of the decay. The advantages of time-resolved measurements compared to steady-state measurements are that multiple decay pathways or dynamic quenching properties can be identified. There are several complex highspeed methods to accurately measure those decays.

3.2.3 Experimental Setup

Time Correlated Single Photon Counting

One technique to get time-resolved fluorescence decays is Time Correlated Single Photon Counting (TCSPC). It is used mostly in biomedical imaging in combination with fluorescence microscopes.[7] Organic molecules often have poorly defined spectral information but easily distinguishable decay lifetimes.[15] Time resolved fluorescence spectroscopy is therefore a good method for the characterization of energy transfers inside a molecule.

Time Correlated Single Photon Counting is a cost effective way to measure time-resolved fluorescence in the picosecond regime. The most important part, apart from the detector, are the actual single photon counting electronics.

Principle (Single Photon Counting)

To visualize the single photon counting process imagine a typical decay. The electronics of the setup divide the time axis into small buckets and collect the photons arriving at a certain delay Δt after the laser pulse in the respective bucket. Via this method this decay can be reconstructed from several single photon measurements.

There are two ways to trigger the signal. The first way is to use a fixed amplitude. This has the disadvantage that for different amplitudes the system would trigger at different times. To circumvent this problem, the buckets are triggered with constant fraction discriminators (CFD) which trigger at the same rise time for different amplitudes.

Setup

Using either a single wavelength 370 nm laser, LDH-P-C-375 (PicoQuant, Germany, with the flippable mirror and the trigger signal from the laser controller) and or one of the Tsunami Ti:Sapphire laser system, with a pulse picker with an integrated frequency doubler (using a PicoQuant PMA-200 photo diode for the trigger signal), a broad wavelength range from 345 nm to 800 nm for TCSPC experiments is available. The detector, PicoQuant PMT Hybrid 06, is a fast hybrid photomultiplier tube with Peltier cooling to reduce the dark count rate which is sensitive in the range of 220 nm to 650 nm. The samples were pipetted into 10x10 mm Suprasil Quartz glass cuvettes from Hellma Analytics. Two fused silica lenses inside a cage system were



Figure 3.9: Principle of Time Correlated Single Photon Counting (TCSPC). The pulses in the middle panel represent the output from a constant fraction discriminator (CFD) where a constant fraction is used to trigger which yields the same trigger time even for different amplitudes. Adapted from [47].

then used to collect the fluorescence in a 90 degree configuration which is subsequently coupled into a 600 μ m diameter FC/APC fiber. FC/APC fibers feature an angled end and are necessary to avoid back reflections inside the fibers and the monochromator.

When measuring the whole spectrum the fiber is attached directly to the detector. If a particular wavelength is deemed to be interesting a McPherson model 2035 scanning monochromator with a 12001/mm grating blazed at 500 nm can be put between detector and the light collection setup. The PMT is connected to a PicoQuant TimeHarp260P single photon counting PCI express card inside the PC set up for the experiment. All measurements were run until the maximum value reached 10000 counts.

Instrumental Response Function

Running a TCSPC experiment typically consists of two parts, first measuring the instrumental response function (IRF) of the system, and afterwards measuring the fluorescence. In the end, a complex fitting function is created by convoluting the IRF with a certain amount of exponential functions.

The IRF is the instrument's response to a zero lifetime sample defined by the number of optics, cuvettes and geometric alignment of the setup. In order to measure the IRF typically a cuvette is filled with a highly diluted colloidal silica solution which acts as a zero lifetime Rayleigh scatterer.[47] The photons of the laser pulses hit the silica spheres and scatter through the setup. Those photons are then measured with the PMT. Depending on the number of lenses used in the optical pathway, cuvette types, detector and of course the electronics a very sharp peak is usually observed as can be seen in figure 3.11(a).



Figure 3.10: Setup of the time correlated single photon counting measurements. Either a single wavelength 370 nm laser with a trigger diode or a Tsunami Ti:Sapphire laser system with a pulse picker with an integrated frequency doubler a broad wavelength range from 345 nm to 800 nm for TCSPC experiments is available. Two fused silica lenses inside a cage system are then used to collect the fluorescence in 90 degree configuration which is subsequently coupled into a 600 µm diameter FC/APC fiber. When measuring the whole spectrum the fiber is attached directly to the fast hybrid PMT detector. If a particular emission wavelength is interesting a McPherson model 2035 scanning monochromator can be put between detector and the light collection setup. The PMT is connected to a PicoQuant TimeHarp260P single photon counting PCI express card inside the PC set up for the experiment.

Decay

Once the IRF is measured, the cuvette containing the colloidal silica solution is replaced with cuvette containing the actual sample of which the time-resolved fluorescence is going to be measured. Without changing the laser power, as this would change the IRF shape which is important for the fitting process, the sample is measured and a decay obtained which should look similar to figure 3.11(b). The laser dominates the first part of the curve whereas the remaining part is dominated by a slower decay process back to the baseline.

Fitting

For fitting the baselines are subtracted from the IRF and the decay measurement. Usually the baseline of the IRF is lower than the one from the decay measurements. The reason for this is that the IRF is much sharper and reaches 10000 counts faster than the broader decay measurements.

Afterwards the IRF is normalized to one, yielding the instruments photon time arrival proba-



Figure 3.11: a) IRF of the TCSPC setup. FWHM $\approx 55 \, ps$ and b) a typical TCSPC decay curve consisting of multiple decay processes.



Figure 3.12: TCSPC decay data in red, the Instrumental Response Function in blue and the reconvolution fit in orange. Using three decay components for TMGquCu-complexes a good fit can be achieved.

bility density. This makes sense as at the end, the one, all the photons of the integration interval have reached the detector. Now the number of expected exponential decays has to be selected. Those are then convoluted with the IRF according to equation 3.5 and used as the fitting function for the decay.

$$I(t) = \int_{-\infty}^{t} IRF(t') \sum_{i=1}^{n} A_i e^{-\frac{t-t'}{\tau_i}} dt'$$
(3.5)

with A_i the amplitude of the ith decay at time zero and τ_i the lifetime of the ith component. Combining IRF, Decay and fit in figure (3.12) one can see that this method leads to a very good representation of the measured data. All fits and errors were obtained using the PicoQuant FluoFit software.

3.3 X-Ray Absorption Spectroscopy

3.3.1 Sample Preparation

All copper complexes measured at the PETRA III beamline P11 were dissolved in 99,8% Acetonitrile (abcr GmbH, Karlsruhe) to a concentration of 10 mM. Future experiments will be done in Chromasolv Plus Acetonitrile (Sigma-Aldrich Laborchemikalien GmbH, Seelze) to avoid impurities in the solvent. For the Diamond Light Source beamline B18 the samples were either been used in powder or in liquid form.

3.3.2 Synchrotrons

Synchrotrons are ring accelerators for electrons, positrons, protons or heavier ions. Usually the particles are accelerated to almost the speed of light in a pre-accelerator which is called an injector due to the fact that it injects the particles into the actual storage ring. Only electron synchrotrons have been used for measurements in this work, so this chapter will only focus on synchrotrons accelerating electrons.



Figure 3.13: PETRA III setup. For the experiment at P11 the ring is operated in "40 bunch mode". This yields a time difference of 192 ns between the electron bunches and the emitted synchrotron radiation. Adapted from [23].

Electrons are generated using an electron gun and afterwards accelerated using a linear accelerator which is equipped with radio frequency cavities in which the electrons are accelerated even more. When the electrons reach energies in the MeV region they are injected into a booster ring in which the electrons are accelerated to almost the speed of light. When the energy of the electrons reaches the GeV region they are injected into the storage ring in which they circulate for a few hours. Due to the bending magnets used to keep the electrons in the storage ring each time they pass such a magnet the electrons are accelerated and emit so called Synchrotron Radiation (SR) tangential to the circle the electrons move on. The geometric shape of the emitted electrons is a small cone with a vertical angular width of $1/\gamma$ with $\gamma = E/mc^2$ where E is the energy of the electron and mc^2 the rest energy of it. To compensate for the energy losses due to the acceleration of the electrons, new electrons have to be injected into the storage ring

from time to time.

Important properties of a synchrotron are photon flux, intensity, brilliance, energy bandwidth and emittance.

The photon flux F stands for the overall number of photons per second in a beam:

$$F = \frac{\# \ photons}{s} \tag{3.6}$$

The *intensity* I is basically the photon density per second for a specific area [16]:

$$I = \frac{\# \ photons}{s \cdot mm^2} \tag{3.7}$$

The brilliance B describes the quality of the synchrotron source and is given by [16]:

$$B = \frac{\# \ photons}{s \cdot mm^2 \cdot mrad^2 \cdot 0.1\% BW}$$
(3.8)

which is the flux per source area per opening angle for a given energy bandwidth (BW). The energy bandwidth is defined as 0.1% of the photon energy [16]:

Energy
$$BW = \frac{\Delta E}{E} = 10^{-3} = 0.1\% BW$$
 (3.9)

The emittance is defined as the product of opening angle and source size. A low emittance equals high brilliance.^[23]

3.3.3 Experimental Setup

Beamline P11 at PETRA III

At PETRA III the magnetic field inside the radio frequency (RF) cavities oscillates with a frequency of $f_{RF} = 500 \text{ MHz}$ [23, 86], creating so called buckets which can be used to transport electrons inside the storage ring. The revolution frequency f_{rev} is given by the circumference of the ring (2304 m) and the speed of the electrons which is close to c:

$$f_{rev} = \frac{c}{\text{circumference}} \approx 130 \,\text{kHz}$$
 (3.10)

which gives for the number of buckets:

$$n_{\rm buckets} = \frac{f_{RF}}{f_{rev}} \approx 3840 \tag{3.11}$$

Those buckets can be filled with electron bunches. The length of a bunch can be determined by measuring the pulse duration of the emitted X-ray bunch and is found to be approximately 100 ps FWHM. PETRA III can be run in different operation modes with either 40, 60, 240 or 960 bunches. For the 40 bunch mode used for the measurements in this thesis the time gap between two adjacent bunches is 192 ns.

The P11 beamline covers an energy range of 2.4 - 30 keV. The first optical element at P11 is a LN₂ cooled double-crystal monochromator. This enables the selection of specific wavelengths. It consists of two Si-111 and Si-311 crystals with an energy resolution of $\Delta E/E = 1.3 \cdot 10^{-4}$ and $\Delta E/E = 0.28 \cdot 10^{-4}$ respectively.[23]



Figure 3.14: Jet setup at PETRA III beamline P11. The whole setup is mounted on a hexapod stage for easy alignment in the X-ray beam. A base plate on top of the hexapod holds the jet setup, the optics for focusing the laser on the jet and an APD for fluorescence detection. Both the jet and the APD are mounted on xyz-stages and the alignment is done using an on-axis video microscope. Image taken from [23].

The XAFS setup of the P11 experimental hutch can be seen in figure 3.14. A Pharos femtosecond pulsed laser system (Light Conversion, Vilnius, Lithuania) with a repetition rate of 83,3 MHz was used. The oscillator provides laser pulses with a wavelength of 1030 nm, a power of around 1800 mW and a pulse power of 22 nJ. Using a sophisticated synchronization system described in detail in the PhD thesis of Benjamin Dicke [23], the laser is synchronized to the Petra III bunch clock, leading to a repetition rate of 130 kHz, a pulse power of up to 46 μ J and a pulse duration of lower than 180 fs. Using the harmonic generator HIRO of the Pharos laser the third harmonic with a wavelength of 343 nm is generated and was been used for the experiments.[23]

The whole setup is mounted on a hexapod stage for easy alignment in the X-ray beam. A base plate on top of the hexapod holds the jet setup, the optics for focusing the laser on the jet and an APD for fluorescence detection. Both the jet and the APD are mounted on a xyz-stage for perfectly aligning the jet to the X-ray beam and the laser beam and the APD to the best fluorescence signal. The alignment is done using an on-axis video microscope.[23]



Figure 3.15: a) Glass nozzle mounted in Swagelok adapter. b) Microscope image of a glass nozzle tip. Image taken from [23].

The jet setup consists of a reservoir that is connected via pipes to a mzr-4605 micro-annular gear pump (HNP Mikrosysteme GmbH, Schwerin) delivering the pulsation-free liquid flow and low shear stress needed for a stable jet. A glass nozzle, which is mounted in a Swagelok system

with a plastic ferrule (see figure 3.15a), with an opening between $30 \,\mu\text{m}$ and $300 \,\mu\text{m}$ (see figure 3.15b for the nozzle tip) is used to produce the jet.[23]

Beamline B18 at Diamond Light Source

The circumference of the ring of Diamond Light Source (DLS) is 561.6 m [85], thus giving us a revolution frequency of around 533 kHz

$$f_{rev} = \frac{c}{\text{circumference}} \approx 533 \,\text{kHz}$$
 (3.12)

which gives for the number of buckets $(f_{RF} = 500 \text{ MHz} [85])$:

$$n_{buckets} = \frac{f_{RF}}{f_{rev}} \approx 938 \tag{3.13}$$

This is only for comparison with P11 as no time-resolved measurements have been done at DLS.

The B18 default setup consists of a 30 cm-long ionization chamber for intensity monitoring and transmission measurements and a 9-element Ge detector. In addition a 4-element silicon drift detector and a gas microstrip are available for fluorescence experiments at low energies. Also a high resolution Si-microstrip detector covering 60 degrees can be used.

Compared to the P11 beamline, B18 covers an 5 keV higher energy range from 2.4 keV to 35 keV thus covering K-edges from phosphorus to iodine, and LIII-edges from yttrium to uranium. The first optical element at B18 is, as well as at P11 a LN₂ cooled double-crystal monochromator for further wavelength selection.[20, 21]

For the low temperature studies a cryostat with liquid nitrogen cooling was used. The sample has been mounted in a custom made sample holder (see figure 3.16(b)). For this the sample powder was compacted, sealed with kapton film and always kept in liquid nitrogen (see figure 3.16(c)).



(a) B18 beamline layout at the Diamond Light Source



(b) Sample holder for B18



(c) B18 sample holder in liquid nitrogen

Figure 3.16: a) B18 beamline layout. The X-ray beam enters from the left side and passes several optical elements in the optics hutch until it hits the sample position in the liquid nitrogen cryostat in the experimental hutch. The setup is remote-controlled from the control room. [6, 20, 21] b) Sample holder for Diamond Light Source with a cuvette in a plastic bag. The powder is fixed between two Kapton foils and then inserted into the liquid nitrogen cryostat and c) the sample holder with mounted cuvette in liquid nitrogen

Chapter 4

Results and Discussion

In this chapter, several spectroscopic measurements on copper complexes with the TMGqu ligand will be presented. The aim of this work was to characterize modern synthetic copper complexes which mimic their natural models and to understand their structure and their physical and chemical properties. To achieve this, several optical spectroscopic methods have been used.

Resonant Raman spectroscopy yielded characteristic energy-dependent spectra of the complexes. In addition the influence of different solvents and counter ions has been investigated. Work on extending the setup for time-resolved measurements has begun and first test measurements have also been conducted. A new setup for measuring time-resolved fluorescence with a time-resolution of 25 ps has been established and extended for a wide range of measurements. With the use of a McPherson monochromator it is possible to analyze the wavelength dependence of the time constants. A pulse picker with integrated frequency doubler allows for using slower repetition rates of 8 MHz and lower compared to the 80 MHz of the used Tsunami laser system. This makes it possible to use the whole frequency-doubled wavelength range for slower decay processes and offers the possibility to compare the results with the energy-dependent Raman measurements. The last used method has been XAFS to determine and validate the oxidation state and the geometry of the copper complexes. Measurements have been conducted at PETRA III in Hamburg using a liquid jet delivery system to minimize radiation damage of the sample and at the Diamond Light Source using liquid nitrogen cooled powder samples.

4.1 Samples

The (bis)chelate complexes used are mono-copper complexes with either 1,1,3,3-Tetramethyl-2-(quinoline-8-yl)guanidine (TMGqu) [36] or N-(1,3-Dimethylimidazolidine-2-ylidene)quinoline-8-amine (DMEGqu) [36, 40] as hybrid guanidine-quinoline ligands (see figure 4.1).

Both ligands show a comparable absorption spectrum with the DMEGqu absorption peaks shifted to lower wavelengths (see figure 4.3(a)). The central copper ion has an oxidation state of either Cu^I or Cu^{II} where the former shows a distorted tetrahedral and the latter a distorted square-planar coordination geometry.[35]

This leads to an interesting similarity between both complexes which is called "entatic state" geometry and both complexes are so distorted the resulting structures only show a twist of roughly twenty degrees to each other (see figure 4.4(b)) making them ideal complexes for detailed spectroscopic studies.



Figure 4.1: Chemical structure of the hybrid guanidine-quinoline ligands a) 1,1,3,3-Tetramethyl-2-(quinoline-8-yl)guanidine (TMGqu) and b) N-(1,3-Dimethylimidazolidine-2-ylidene)quinoline-8-amine (DMEGqu). Adapted from [36, 40].



Figure 4.2: Chemical structure of the counter ions used. a) Hexafluorophosphate and b) Trifluoromethanesulfonate.



Figure 4.3: UV-Vis absorption spectra of a) the hybrid guanidine-quinoline ligands TMGqu and DMEGqu and b) UV-Vis absorption spectra of the different oxidation states of the TMGqu copper complex. Measurements conducted and kindly provided by the group of Sonja Herres-Pawlis.



Figure 4.4: a) Molecular structure of (TMGqu)₂Cu and b) Superimposed molecular structures of Cu^I darker with solid bonds, Cu^{II} lighter with dashed bonds. You can clearly see that the two structures are twisted toward each other by around twenty degrees.[35]

4.2 Raman Spectroscopy

4.2.1 Planning the Measurements

The fundamental laser line of the Tsunami system which has been used can be tuned from 700 nm to 1050 nm. The GWU flexible harmonics generation unit has two mirror sets with different coatings for two parts of this range. The "short" set comprises the range from 720 nm to 850 nm while the "long" set the range from 840 nm to 1000 nm. Although the Tsunami's fundamental range is the same for both sets, only the above mentioned parts are shown in figure 4.5.

The 2ω range for the "short" option which was used for the experiments spans the range from 360 nm to 425 nm and the frequency tripled 3ω 240 nm to 283 nm. The Krypton laser could provide additional wavelengths which can be seen in figure 4.5 but was dysfunctional while the measurements were conducted.

 Table 4.1: Chosen wavelengths for energy dependent Raman measurements.

ω [nm]	2ω [nm]	3ω [nm]	
721.1	361.2	240	
	374.8	259.5	
	417.3	277.8	

As can be seen from the absorption spectra of the complexes (see figure 4.3(b)) compared to the absorption spectra of the ligands there are additional peaks in the range of 390 nm for the Cu^{II} and 440 nm for the Cu^I. It was considered interesting to probe those ranges so the following wavelengths for the sample scanning were chosen:



Figure 4.5: Overview of the possible laser wavelengths in the Hamburg optics lab. When using the "short" mirror set in the FHG unit the Tsunami wavelengths from 720 nm to 850 nm are usable. Higher harmonics are marked as 2nd and 3rd. When changing the mirror set to the "long" option (Tsunami wavelengths 840 nm to 1000 nm are usable), the wavelengths in the green boxes are obtainable. Higher harmonics are again marked as 2nd and 3rd. Although the Tsunami's fundamental range is 700 nm to 1050 nm only the usable parts for the respective FHG mirror sets are shown. Additionally all Krypton and frequency doubled Krypton wavelengths are depicted as blue bars.

While the 3ω range should mostly cover the ligand absorption region, the 2ω range should probably cover the metal-to-ligand (MLCT) and ligand-to-metal charge transfer (LMCT) region. The ω region is there for the completeness of the study, but as seen in the absorption spectra of the complexes, we do not expect particularly interesting results in this region.

4.2.2 Measurements

For the resonance Raman study, the samples were measured at several wavelengths. Acetonitrile (MeCN) and Dichloromethane (DCM) were tested for their suitability as solvent and their influence on the samples. Spectra for each solvent were recorded at all wavelengths and the relative peak intensities were locked for further fitting of the Raman spectra of the samples at the same wavelength.

As can be seen in figure 4.6, both solvents unfortunately show peaks in all regions through the spectrum. The region up to 200 wavenumbers is stray laser light leaking into the measurement window and is taken care of in the following fit procedure. DCM shows a distinct peak at 300 cm^{-1} followed by a double peak structure at 740 cm^{-1} and 780 cm^{-1} , followed by a rather small peak at 900 cm^{-1} which seems to be MeCN residue in the cuvette. In the higher wavenumber region DCM shows two weaker peaks at 1190 cm^{-1} and 1430 cm^{-1} . MeCN of course shows the same laser leak in the very low wavenumber regions but compared to DCM shows only three distinct peaks at 390 cm^{-1} , 900 cm^{-1} and 1390 cm^{-1} . Also there is a weak peak at around 750 cm^{-1} .

As an exemplary spectrum figure 4.7 shows a part of the Raman spectrum of TMGquCu^I for an incident photon energy of 417.3 nm. Laser stray light in the region up to 200 wavenumbers



Figure 4.6: a) Raman spectrum of DCM and b) Raman spectrum of MeCN. The left peak up to 200 wavenumbers is laser stray light leaking into the measurement window.

is once again observed and due to longer integration times for the copper samples is higher in intensity as the solvent spectra. Furthermore the solvent peaks of MeCN are clearly visible at 390 cm^{-1} and 900 cm^{-1} . The step at around 500 cm^{-1} in figure 4.6(b) is the glass signal of the cuvette which covers the signal of the sample making only features with higher wavenumbers accessible in this study.



Figure 4.7: Raman spectrum of TMGquCu^I @ 417 nm in MeCN and DFT calculated Raman vibrational modes for each peak for the TMGquCu^I complex at 417 nm incident photon energy.[35]

Starting at 540 cm^{-1} the first clearly visible peaks of the sample appear, followed by a double peak structure at around 620 cm^{-1} and 640 cm^{-1} . Another peak can be seen at around 700 cm^{-1} followed by a triple peak structure around 800 cm^{-1} . With DFT calculations it was possible to assign these peaks to vibrations in the molecule.[35] As can be seen in figure 4.7, the peak structure around 800 cm^{-1} can be assigned to core vibrations of the copper and the nitrogen atoms of the guanidine part of the ligand.

When remembering the Raman spectra of the solvents, DCM shows a very intensive double peak structure in the range of those core vibrations, thus making it impossible to analyze them in more detail. For the following resonance Raman study, MeCN was chosen as solvent for the above mentioned reasons. The influence of DCM compared to MeCN will be analyzed later in this work.

The next influence on the measurements besides the solvents could be the counter ions. As shown in figure 4.2 either PF_6^- or TfO^- were used for the complexes. To investigate their influence XAFS and Raman measurements with different ions were conducted. As shown in figure 4.8(a), counter ions do not influence Raman or XAFS measurements, so for all the following Raman spectra the triflate (TfO^-) counter ion has been used. According to the XAFS measurements in figure 4.8(b) it is also reasonable to measure the samples in solution as the state of matter does not change the molecular structure of the complexes. As large single crystals of the samples are hard to obtain, this simplifies the Raman measurements considerably.



Figure 4.8: a) Raman spectrum of TMGquCu^ITfO (top) and TMGquCu^IPF₆ (bottom). As the spectra only slightly differ for the solvent peak denoted with a star, it can be assumed that counter ions do not influence the Raman spectrum and b) XANES spectra of TMGquCu^I and TMGquCu^{II} for solid and samples solved in MeCN. As can be seen, the complex structure is not influenced by the solvent.[35]

For the resonance Raman study, the complexes were measured as mentioned in table 4.1. 240 nm and 720 nm have been omitted in the following analysis. The signal for 240 nm was too weak and due to this the silicon optimization was not possible. The measuremnts at 720 nm did not show any peak intensity and were set to zero for the peak analysis.

All spectra were fitted and the glass and stray light features were taken into account by

fitting them and thus removing their influence on the peak intensities from the sample features. The peak intensities were then corrected by the wavelength dependent-absorption of the samples with the following equation [32]:

$$I_{cor} = \frac{I_{raw}}{(1 - exp(-2.3 \cdot \epsilon \cdot c \cdot d))}$$

$$\tag{4.1}$$

where I_{cor} is the absorption corrected intensity of the respective peak, I_{raw} the measured peak intensity, ϵ the molar extinction coefficient, c the concentration (10 mM) of the sample and d (150 µm) the length of the path the light travels in the solution. The denominator of the correction term is shown in table 4.2 for all incident photon energies.

Table 4.2: Denominator of equation (4.1) and correction factor for Raman peak intensities.

Sample	$259.5\mathrm{nm}$	$277.8\mathrm{nm}$	$361.2\mathrm{nm}$	$374.8\mathrm{nm}$	$417.3\mathrm{nm}$
$\begin{array}{c} TMGquCu^{I} \\ TMGquCu^{II} \end{array}$	0.9999999 0.9999999	$0.998138 \\ 0.999868$	$0.919291 \\ 0.927322$	0.891177 0.957968	0,894544 0.825296

As can be seen in figure 4.9, Cu^I and Cu^{II} complexes show different Raman behavior at the same incident photon energy which is expected due to their different absorption spectra as seen in figure 4.3(b).



Figure 4.9: a) Raman spectrum of TMGquCu^I at 278 nm incident photon energy (top) and Raman spectrum of TMGquCu^{II} at 278 nm incident photon energy (bottom). One can clearly see that for this excitation wavelength the peaks for Cu^{II} are more pronounced, especially in the region of 450 to 750 wavenumbers where one can barely see the peaks for the Cu^I sample.
c) Raman spectrum of TMGquCu^{II} at 417 nm incident photon energy (bottom). Contrary to the spectra at 278 nm incident photon energy the Cu^I sample shows more distinct peaks, especially the region around 800 wavenumbers is much better defined.

The difference in the resonance behavior can be seen in more detaile in figure 4.10. While the Cu^{I} samples show their resonance in the region of 3.4 eV, the Cu^{II} samples show a resonance slightly shifted to lower energies of 3.2 eV. As both resonances are around the same incident photon energy it can be assumed that they connect both oxidation states within a chargetransfer process. Further DFT calculations confirm this behavior.[39] For Cu^{I} it is a metalto-ligand charge transfer (MLCT) and the corresponding transition of the Cu^{II} complex is a complementary ligand-to-metal charge transfer LMCT.[35]



Figure 4.10: a) Peak identification for TMGquCu^I at 417 nm incident photon energy and b) peak identification for TMGquCu^{II} at 278 nm incident photon energy. c) and d) show the absorption-corrected peak intensities for the peaks from a) and b) for TMGquCu^I and TMGquCu^{II} respectively. Furthermore, the molar extinction coefficient has been plotted for both complexes in light gray. One can clearly see that the vibration modes at 788 cm⁻¹ and 815 cm⁻¹ come into resonance at around the same incident photon energy therefore it can be assumed that they connect both oxidation states within a charge-transfer process. [35]

As can be seen in table 4.3, important geometric properties of the complexes change. The Cu-N_{imine,gua} bond length, which is 2.09 Å for Cu^I and 1.97 Å for Cu^{II} clearly move towards each other. The chelate planes (\triangleleft (CuN₂,CuN'₂)) also twist towards each other supporting the initial hypothesis that the change between the two oxidation states can be optically triggered. In the following chapter time-resolved XAFS and fluorescence measurements will be presented which will further investigate the dynamics of charge transfer processes.

 Table 4.3: Changes of important geometric properties of the two TMGqu-complexes when being excited.

 One can clearly see that the two excited complexes move towards each other in bond length as well as chelate plane angles.

oxidation state	$\operatorname{Cu-N_{imine,gua}}$ bond length	\sphericalangle (CuN $_2$,CuN' $_2$)
Ι	$2.09{ m \AA}$	68 °
Iex	2.01 A	61 °
II	$1.97{ m \AA}$	43°
Π^{ex}	$2.06\mathrm{\AA}$	64 °

Paper I Catching an Entatic State - A Pair of Copper Complexes

Alexander Hoffmann, Stephan Binder, Anton Jesser, Roxana Haase, Ulrich Flörke, Manuel Gnida, Marco Salomone Stagni, Wolfram Meyer-Klaucke, Benjamin Lebsanft, Lara Elena Grünig, Simon Schneider, Maryam Hashemi, Arne Goos, Alina Wetzel, Michael Rübhausen, and Sonja Herres-Pawlis

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Catching an Entatic State—A Pair of Copper Complexes**

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Dedicated to Professor Bernt Krebs on the occasion of his 75th birthday

Abstract: The structures of two types of guanidine–quinoline copper complexes have been investigated by single-crystal X-ray crystallography, K-edge X-ray absorption spectroscopy (XAS), resonance Raman and UV/Vis spectroscopy, cyclic voltammetry, and density functional theory (DFT). Independent of the oxidation state, the two structures, which are virtually identical for solids and complexes in solution, resemble each other strongly and are connected by a reversible electron transfer at 0.33 V. By resonant excitation of the two entatic copper complexes, the transition state of the electron transfer is accessible through vibrational modes, which are coupled to metal–ligand charge transfer (MLCT) and ligand–metal charge transfer (LMCT) states.

C opper is one of the most important redox-active metals and plays a central role in many biological processes.^[1] Blue copper electron-transfer proteins are nature's workhorses for electron transfer (ET). They use copper as a one-electron relay that shuttles between the cuprous and cupric oxidation states. Their Cu^{11/1} reduction potentials span a large window $(E^{\circ\prime} = 0.18 \text{ to } > 1 \text{ V}$ versus NHE (normal hydrogen electrode)),^[2] which tailors these proteins to interact with a wide variety of ET partners. The inner coordination sphere most directly affects the redox properties of metal ions.^[3] Hence, tuning the Cu^{11/1} redox couple is central for electron transfer in nature and also important in synthetic complexes for catalytic applications.^[4-6] There are multiple factors governing the redox potential, including the effects of the first coordination sphere such as geometric constraints enforced by the ligand sphere (tetrahedral versus square-planar coordination) and ligand donor atoms (σ - and/or π -donation), as well as second-coordination-sphere effects.^[7-11]

Already in 1968, Vallee and Williams coined the term "entatic state" (also called rack-induced state), defined as a "catalytically poised state intrinsic to the active site".^[12] This term has been intensively discussed during the last decades.^[7,13-15] Rorabacher et al. specified it to be an electronic entatic state rather than a simple geometric constraint physically imposed upon the active site by the protein matrix.^[16] Hodgson et al. proved with X-ray absorption spectroscopy (XAS) methods that the concept of a rackinduced state might be not valid as the protein imposes almost no strain on the copper coordination.^[17] Theoretically, it was proven that Cu^{II} prefers square-planar and square-pyramidal coordination but that π -donor ligands lead to stabilization of trigonal distorted geometries.^[18] Recently, Vila et al. found that the entatic state does not require the ligand to have a preformed metal-binding site. They identified metal binding as a major contributor to the conformational rigidity of copper centers involved in electron transfer which reconciles the seemingly contradictory requirements of a rigid center for electron transfer and an accessible, dynamic site for in vivo copper uptake.^[19] In blue copper centers, the entatic state is currently regarded as a "soft entatic state",^[20] whereas the whole concept has been condensed into an "energization due to a misfit between ligands and metal ions."^[21]



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Supporting information for this article (including details on materials and methods, synthetic procedures, Raman measurements, XAS spectroscopy, cyclic voltammetry, square-wave voltammetry, and DFT details on Raman assignment and excited-state calculations) is available on the WWW under http://dx.doi.org/10. 1002/anie.201306061.

Angewandte Communications

Here, we report a series of bis(chelate) Cu^I and Cu^{II} complexes in which the cationic units have very similar structures even though Cu^I and Cu^{II} complexes generally prefer tetrahedral and square-planar environments, respectively. Besides the structural study of single crystals in the solid state, we provide insights into the structure in the liquid phase that we obtained from XAS data of complexes in solution. A resonance Raman study of Cu^I and Cu^{II} complexes in solution indicates that both complex types come into resonance at a similar energy around 3.2-3.4 eV. We found a vibrational mode that couples vibronically the optical charge-transfer excitation with the distortion along the reaction coordinate, leading from the Cu^I to the Cu^{II} geometry. Therefore, we have optical access to a chargeseparated state which mimics the transition state of the innersphere ET. In contrast to reported outer-sphere electrontransfer studies on Cu^{II/I} pairs,^[22] we focus on the photochemically induced charge transfer.

The reaction of tetramethylguanidinoquinoline (TMGqu)^[23] with suitable copper sources yields the series of bis(chelate) Cu^I and Cu^{II} complexes 1-5. The most remarkable feature of these complexes is their structural similarity (Figure 1, Table 1, and Figures S1-S5 in the Supporting Information). For a Cu^I complex, one would generally expect a structure with tetrahedral configuration as found in [Cu- $(\text{tmeda})_2]^+$ complexes (tmeda = tetramethylethylenediamine),^[24] whereas Cu^{II} complexes are square-planar (e.g. $[Cu(tmeda)_2]^{2+}$.^[25] But in the complexes **1–5**, the situation is completely different. The copper centers of all complexes are tetracoordinate through interactions with two chelating guanidine-quinoline ligands. The $\mbox{Cu-N}_{\mbox{\scriptsize gua}}$ distances in the Cu^{I} complexes 1-3 are 0.1 Å longer than those in Cu^{II} complexes 4 and 5. The contraction of the $Cu-N_{au}$ bonds during the formal oxidation is not very pronounced (0.02 Å).

The coordination geometry can be described by a τ factor indicating a square-planar arrangement for a value of 0 and an ideal tetrahedron for a value of 1.^[26] In the Cu^I complexes, we

Table 1:	Key	geometric	parameters	of	complexes	1-	-5
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Figure 1. Superimposed molecular structures of $[Cu(TMGqu)_2]^+$ and $[Cu(TMGqu)_2]^{2+}$ (Cu¹: darker with solid bonds, Cu^{II}: lighter with dashed bonds).

observe a τ of roughly 0.6 indicative of a strongly distorted tetrahedron, whereas in the Cu^{II} complexes τ amounts to 0.4. The angle between the chelate planes Cu-N_{gua}-N_{qu} gives a measure of the tetrahedral character as well: 90° correspond to an ideal tetrahedron and 0° to square-planar coordination. This angle ranges from 65.1 to 68.3° in the Cu^{II} complexes and from 42.5 to 44.6° in the Cu^{II} complexes. This clearly demonstrates that the difference between the two oxidation states results in a twist of approximately 20° between the chelate planes and a shortening of the Cu–N_{gua} bond by 0.1 Å. The guanidine substituents force the ligands to avoid each

	[Cu(TMGqu) ₂]CF ₃ SO ₃ 1	[Cu(TMGqu)₂]PF₀ 2	[Cu(TMGqu) ₂]ClO ₄ 3	$[Cu(TMGqu)_2](CF_3SO_3)_2$ 4	[Cu(TMGqu) ₂](PF ₆) ₂ 5
Bond lengths [Å]					
Cu-N _{imine.gua}	2.065(2), 2.113(3)	2.068(3), 2.095(3)	2.074(3), 2.080(3)	1.959(2), 1.964(2)	1.964(3), 1.964(3)
Cu–N _{au}	1.978(3), 2.003(2)	1.966(3), 1.999(3)	1.998(3), 2.002(3)	1.976(2), 1.975(2)	1.967(3), 1.980(3)
C _{gua} -N _{imine,gua}	1.324(4), 1.321(4)	1.316(4), 1.330(4)	1.319(4), 1.312(4)	1.344(3), 1.347(3)	1.358(4), 1.347(4)
C _{gua} -N _{amine.gua}	1.356(4), 1.359(4)	1.365(5), 1.357(5)	1.362(4), 1.352(4)	1.346(3), 1.343(3)	1.324(4), 1.346(4)
	1.356(4), 1.372(4)	1.363(5), 1.355(5)	1.361 (4), 1.359 (4)	1.340(3), 1.341(3)	1.344(4), 1.344(4)
Bond angle [°]					
N-Cu-N	82.1(1), 81.7(1)	82.6(1), 82.1(1)	82.2(1), 81.8(1)	83.5(1), 83.7(1)	83.6(1), 83.7(1)
Structure factors					
$\tau_{A}^{[a]}$	0.60	0.58	0.60	0.40	0.41
$ ho^{[b]}$	0.97, 0.96	0.96, 0.97	0.96, 0.97	1.00, 0.99	1.02, 1.00
Torsion angles [°]					
⊥ (C _{ma} N ₃ ,CuN ₂)	49.5, 58.6	49.1, 58.5	53.0, 59.2	47.5, 52.1	46.9, 47.2
$\measuredangle(N_{amine}C_3, C_{gua}N_3)$	30.0(av), 29.9(av)	30.1 (av), 27.7 (av)	30.0(av), 29.0(av)	28.3 (av), 31.1 (av)	30.0(av), 28.5(av)
∡(CuN₂,CuN′₂)	68.0	65.1	68.3	42.5	44.6

[a] $\tau_4 = \frac{360^{\circ} - (a+\beta)}{141}$.^[26] [b] $\rho = 2a/(b+c)$ with $a = d(C_{gua} = N_{imine,gua})$, b, and $c = d(C_{gua} - N_{amine})$.^[27]

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Figure 2. Left: Cu K-edge absorption of solid **2** and **5** (solid curves) as well as solutions of **1** and **4** in MeCN (broken curves). Right: Superimposed experimental k^3 -weighted EXAFS spectra of various Cu¹ and Cu¹¹ complexes.

other and sterically restrain the coordination geometry to only small variations, ranging from 68 to 44° between the CuN_2 planes and the corresponding range of the τ value from 0.6 to 0.4.

Since the structural change between Cu^{I} and Cu^{II} is so small, we expected a reversible redox behavior. Cyclic voltammetry proves a reversible oxidation wave for **2** at 0.33 V vs. NHE (Figure S20, left) and square-wave voltammetry shows the 0.33 V oxidation to be a one-electron oxidation step (Figure S20, right).

To characterize the oxidation states we performed XAS spectroscopy on solid samples of 1-5 (see the Supporting Information for details). The solid curves in Figure 3 compare the Cu-K absorption edges of the complexes [Cu- $(TMGqu)_2$]PF₆ (2) and [Cu(TMGqu)₂](PF₆)₂ (5). The edge positions are 8983.3 eV (2) and 8986.8 eV (5), equal to a chemical shift between the two compounds of $|\Delta E| =$ 3.5 eV. The edge positions and the chemical shift identify the oxidation states as Cu^{I} in 1-3 and Cu^{II} in 4 and 5 (Figure S6, Table S1).^[28] The oxidation state assignment is further supported by the edge shapes. Cu^I complexes have a characteristic shoulder or peak in the rising edge (8985 eV and below, assigned as a $1s \rightarrow 4p$ transition).^[28] In contrast, Cu^{II} edges are of rather low intensity in this energy range. The intensity of the "Cu^I feature" can be related to the site geometry. The normalized fluorescence for 2 at 8985.6 eV is 0.65 (Figure 2), indicative of tetracoordinate $Cu^{\rm I}.^{\rm [28]}$ The $Cu^{\rm II}$ state in 5, in turn, manifests itself in a very weak pre-edge peak at 8977.7 eV (Figure 2, left), assignable as a $1s \rightarrow 3d$ transition.^[29] It is apparent that the edge positions, shapes, and features for Cu^I and Cu^{II} are the same for solid and solution samples (Figure 2). Analysis of extended X-ray absorption fine structure data (EXAFS) (Table S2, Figure 2, right) demonstrates that, for a given oxidation state, the structural models for solid and solution samples are identical within the precision of the analysis and do not depend on the choice of counterion. Raman data support the conclusion that the structure in solution is independent of the counterion (vide infra and Figure S9). EXAFS analysis of the complexes **2** and **5** confirms the molecular structures as being tetracoordinate with two nitrogen back-scatterers at 2.01 Å and two at 2.03 Å in Cu^I as well as two nitrogen back-scatterers at 1.95 Å and two at 2.00 Å in Cu^{II} (Table S2).

Furthermore, we performed Raman measurements on the complexes 1, 2, 4, and 5 in MeCN and CH₂Cl₂ solution (Figure 3). UV/Vis measurements (see Figures S10-S17) indicated that a resonance can be expected at approximately 3.4 eV and above 4.0 eV for complexes in either oxidation states. The Raman spectra show a multitude of peaks between 400 and 850 cm⁻¹. By exciting at numerous incident photon energies, we derive the excitation dependence of the Raman peak intensities. A vibrational assignment is made possible by theoretical calculations based on extensive benchmarking.^[30] Figure 4a details the excellent agreement between experimental Raman spectra taken with a nonresonant incident photon energy of 2.97 eV and calculated Raman spectra. It is noteworthy that for complex 1 2.97 eV is clearly in offresonance condition as the sharp resonance is close to 3.4 eV. Figure 4b compares the experimental Raman data for 4 in nearly nonresonant measurement conditions. The Raman resonance energy is shifted by about 0.3 eV (cf. Figure 3c,d),





Figure 3. a) Raman spectrum of 1 in MeCN upon excitation at 2.97 eV. b) Raman spectrum of 4 in MeCN upon excitation at 4.46 eV. c) Dependence of the Raman intensity on incident photon energy for 1 in MeCN. d) Dependence of the Raman intensity on incident photon energy for 4 in MeCN. Colored symbols were used to indicate Raman peaks and their resonance behavior. The gray line denotes the absorption spectrum, whereas the colored curves serve as a guide to eye. Incident photon energies: 1.72 eV, 2.97 eV, 3.31 eV, 3.43 eV, 4.46 eV, 4.78 eV.

putting the spectrum into a preresonance explaining the difference between the calculated with the observed spectra.

We find that selected Raman peaks of both complexes turn into resonance at 3.40 and 4.45 eV (Figure 3 c,d), namely the peaks at 650, 778, and 811 cm⁻¹ for $\mathbf{1}$ (Cu^I) and at 790 and 815 cm⁻¹ for $\mathbf{4}$ (Cu^{II}). Since these vibrations are resonant at similar energies for both complexes, we relate them to vibrations, which connect the crystallographically determined structures of both oxidation states within a charge-transfer process.

Tables S3 and S4 list the geometrical changes during the vibrations for **1** and **4** together with a detailed assignment. For **1**, the vibration at 800 cm⁻¹ can be related to the experimental vibration at 788 cm⁻¹ (purple triangle), which is a Cu–N_{gua} stretching vibration with concomitant twist of the two chelate planes relative to each other. Precisely these two structural changes are the most important distortions between Cu^I and Cu^{II} geometry. For **4**, the peak at 815 cm⁻¹ is assigned as a Cu–N_{gua} stretching vibration as well. Analysis of the excited singlet states attained by resonant excitation at 3.4 eV shows that for Cu^I the twist angle diminishes by 7° and the Cu–N_{gua} bond contracts by 0.07 Å (Figure 4c, **1**^{ex}). In the reverse sense, the excited state of the Cu^{II} complex (**4**^{ex}) displays an increase in the twist angle of 21° and a Cu–N_{gua} bond elongation of 0.1 Å.

DFT analysis^[30] of the optical transition at 3.4 eV of the Cu^I complex reveals that this is a metal-to-ligand charge transfer (MLCT, electron density difference map in Figure 4d). The corresponding transition of the copper(II) complex is a LMCT which is complementary to the MLCT of Cu^I (Figure 4e). Hence, we have successfully identified the vibronic mode that connects Cu^I and Cu^{II}.

Resonance Raman spectroscopy probes the electronic states that are most relevant for the vibrational excitation spectrum. In particular, a vibrational excitation mediating charge transfer will become resonant very close to the energy of the involved electronic charge-transfer transition that connects the involved electronic orbitals.^[31,32] This resonance is expected to be much sharper and better defined in energy than UV/Vis absorptions since the resonance Raman signals are only related to one specific contribution of the charge transfer selected by the specific vibration and by doing so this technique effectively probes the reaction coordinate. Thus, the LMCT and MLCT identified by Raman spectroscopy occur in close proximity to each other as they access the inverse reaction coordinate through complementary chargetransfer processes.

In summary, we present five complexes with very similar coordination midway between tetrahedral and square-planar geometry: The oxidation of Cu^I to Cu^{II} increases the twist angle formed by the CuN₂ planes by only 20°. The two complex types are connected through a reversible electron transfer. X-ray absorption spectroscopy not only verifies the oxidation states of the reported complexes; it is also in excellent agreement with crystallographic data and demonstrates that the structures are independent of the complexes being solid or in solution. Moreover, the structures are independent of the choice of counterions which is supported by Raman spectroscopy. Hence, the coordination geometry is not a result of solid-state effects but inherent to the effects resulting from the balance between electronic and steric effects. Raman spectroscopy in solution allows access to the reaction coordinate of the electron transfer. Both complex types show resonance at an incident photon energy of 3.4 eV. DFT analysis reveals that at resonance a vibrational mode of $Cu-N_{gua}$ stretching and chelate angle torsion couples with an MLCT from Cu^I to Cu^{II} and an LMCT from Cu^{II} to Cu^I. This proves that the ET transition state is optically accessible and that the concept of ligand restrictions imposed upon copper coordination is very useful for the generation of electrontransfer models.



Figure 4. a) Comparison of nonresonant experimental (black) Raman spectrum at 2.97 eV and theoretical (red) Raman spectrum of 1. b) Comparison of nonresonant experimental (black) Raman spectrum at 2.97 eV and theoretical (red) Raman spectrum of 4. c) Reaction coordinate between Cu¹ and Cu¹¹ and the optically attained excited states. d) EDDM of the Cu $d_{z^2} \rightarrow \pi^*$ transition (light to dark). e) EDDM of the $\pi \rightarrow$ Cu d transition (light to dark)

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4.3 Time-Resolved Spectroscopy

Time-resolved spectroscopy can help to understand the dynamic processes involved in charge transfer processes. To verify the changes happening upon optical excitation, time-resolved pumpprobe XAFS spectroscopy has been used to determine the temporal structural changes in the complexes.

To bridge the gap between the highly concentrated solutions used at P11 for the XAFS and Raman measurements and the lower concentrations typically used for fluorescence measurements, an energy-dependent time-resolved fluorescence spectroscopy setup has been established as part of this work and has been used to determine whether the fluorescence time constants also show the same kind of resonance behavior as has been found in the resonance Raman measurements.

4.3.1 Planning the Measurements

The resonance Raman measurements revealed a resonance of the Cu-N bonds around 360 nm. The closest wavelength of the PHAROS laser system at the PETRA P11 beamline to that is the frequency tripled 3ω at 343 nm. With a laser pulse energy in the μ J region and an average power of up to 1 W it was used for the pump-probe XAFS measurements.

The wavelengths for the fluorescence measurements are limited to the 2ω region of the Tsunami "Short" option by the frequency doubler of the pulse picker. This means that wavelengths from around 360 nm to around 420 nm are usable, providing access to the absorption maximum of the Cu^{II} complex at around 390 nm and the region between the two absorption maxima of the Cu^I complex at around 325 nm and 440 nm (see figure 4.11(b)). It also makes it possible to measure both right flanks of the absorption maxima of the ligands at around 340 nm (see figure 4.11(a)).



Figure 4.11: UV-Vis absorption spectra of a) the hybrid guanidine-quinoline ligands TMGqu and DMEGqu and b) UV-Vis absorption spectra of the different oxidation states of the TMGqu copper complex both with the "Short" 2ω region (green area) and the used 3ω 343 nm laser line (yellow) at the P11 beamline. Measurements conducted and kindly provided by the group of Sonja Herres-Pawlis.

The wavelengths were chosen to span the whole available region while sticking closely to the ones in the Raman study as well as the resonance wavelength around 366 nm found there. See table 4.4 for the exact values.

$ \begin{array}{c} {\rm Fluorescence} \\ {\bf 2}\omega {\rm wavelengths} [{\rm nm}] \end{array} \end{array} $	$\begin{array}{c} {\bf Raman} \\ {\bf 2}\omega \ {\bf wavelengths} \ [{\bf nm}] \end{array}$
365.3	361.2
374.3	374.8
389.2	-
409.4	417

Table 4.4: Chosen incident photon energies for fluorescence and Raman measurements.

To find out whether there are more decay processes involved, the fluorescence emission from the complexes was analyzed for several wavelengths. As can be seen in figure 4.19, the chosen wavelengths 450 nm, 470 nm, 490 nm, 510 nm, 530 nm and 550 nm cover both the left and right flank of the emission spectrum.

4.3.2 Measurements

Time-Resolved XAFS

As the laser system at P11 only allows for frequency doubled or tripled energies of the PHAROS the frequency tripled 343 nm line was used at a laser power of around 150 mW. The laser and X-ray beam were aligned to the liquid jet right below the glass nozzle, so no oxidation of the sample could take place before excitation.

Figure 4.12 shows energy scans where the monochromator shifts the energy by a fixed amount, from 8950 eV to 9250 eV, to cover the copper K-edge and the XANES region. TMGquCu^I ground state (blue) and excited state (black dots) as well as the TMGquCu^{II} ground state (red) have been measured.

For the TMGquCu^I ground state, the edge starts to rise at 8977.5 eV and shows the distinct Cu^{I} feature at 8985 eV (assigned as a 1s \rightarrow 4p transition)[43], in good agreement with other publications.[26] The TMGquCu^{II} ground state copper K-edge edge is shifted by 3.5 eV to 8981 eV. The pre-edge peak at 8977.5 eV and the shifted shoulder to 8987 eV is characteristic for the Cu^{II} oxidation state.[26] The transient for the TMGquCu^I excited state is depicted in green, showing the edge shift by a negative value where the Cu^{I} feature starts before the Cu^{II} feature and a positive value where the Cu^{II} curve is above the Cu^{I} curve.

Upon excitation with the laser, the Cu^I complex is excited to an energetically higher level. The XAFS spectrum is measured at a delay time where most of the Cu^I is in the excited state. This is done by setting the X-ray energy to the negative maximum of the transient, here 8984 eV, and measuring the transient intensity while changing the offset between X-ray beam and laser. This gives a time-resolved plot of the excited state which is shown in figure 4.12. The TMGquCu^I excited state almost perfectly overlaps with the TMGquCu^{II} ground state, which can also be verified by looking at the transient between both absorption curves (black line). This nicely confirms the optical trigger which has been predicted by the resonance Raman measurements. Unfortunately it has not been possible to excite the Cu^{II} sample and reverse the process to obtain the Cu^I oxidation state.

In order to successfully verify this transition further measurements and most likely detector sensitivity improvements as well as improvements in time-resolution have to be made.



Figure 4.12: The top graph shows the Cu^{I} (blue) and Cu^{II} (red) ground state XANES spectrum as well as the excited state Cu^{I} spectrum (black dots). As can be clearly seen, the excited state of $TMGquCu^{I}$ almost perfectly overlaps the spectrum of $TMGquCu^{II}$, confirming the Raman measurements and DFT calculations. The shifted white line by around 100 eV is related to the expected structural distortions between the Cu^{I} and Cu^{II} complexes and a bond length contraction of the $Cu-N_{gua}$ bonds. The bottom graph shows the transient signal of the two ground state spectra (black line) and the transient signal of the excited Cu^{I} state and the Cu^{I} ground state (green). To be published, see Appendix B5.

To obtain the time-resolved decay data the X-ray energy is set to the maximum of the transient signal and the delay between X-ray beam and laser beam is changed in small steps and the transient intensity is recorded. The decay constants of the excited state are then derived from a fit of the time-resolved transient measurements (see figure 4.13).

These show two distinct components (see table 4.5) for the relaxation process. One can also clearly observe quenching effects as the decay times shorten for higher concentrations. To verify and further examine these decay time constants, time resolved fluorescence measurements have been conducted for lower concentrations.

	$1.0\mathrm{mM}$	$2.0\mathrm{mM}$	$5.0\mathrm{mM}$
$ au_1$	$130\mathrm{ps}$	$124\mathrm{ns}$	$106\mathrm{ps}$
$\Delta \tau_1$	$35\mathrm{ps}$	$20\mathrm{ps}$	$20\mathrm{ps}$
$ au_2$	$6.3\mathrm{ns}$	$(7.9\mathrm{ns})$	$3.4\mathrm{ns}$
$\Delta \tau_2$	$2.5\mathrm{ns}$	$(6.5\mathrm{ns})$	$2.1\mathrm{ns}$

 Table 4.5: Transient decay times for different sample concentrations. Collisional quenching effect can clearly be observed.



Figure 4.13: Decay times of the excited TMGquCu^I state from a XAFS delay scan at the maximum transient for several sample concentrations. Collisional quenching effects can be observed as higher concentrations lead to faster decay times. To be published, see Appendix B5.

Time-Resolved Fluorescence

Different wavelengths were used for the time-resolved fluorescence measurements. As for the Raman measurements, the solvents play a huge role for fluorescence. In figure 4.14(a), distinct Raman features of the solvent can be seen on the left flank of the emission spectrum. In addition the main laser wavelength, 410 nm and the residual of the fundamental (820 nm) can be seen. As the decay times in the region of the Raman peaks are independent of the fluorescence lifetime, those regions must be excluded from further analysis. As a side note it should be mentioned here that decay times in dichloromethane are significantly slower due to the influence of the dichloromethane. All following measurements were conducted using Acetonitrile.

The emission spectrum of the Cu^{I} complex shows a maximum at around 520 nm and an almost symmetric profile with a slight broadening on the right side. The maximum of the Cu^{II} spectrum is slightly shifted to the right by around 30 nm to 550 nm, but otherwise appears similar to the Cu^{I} spectrum, featuring the same broadening on the right side. The intensity of Cu^{I} is lower by a factor of around two compared to the TMGqu emission and the Cu^{II} emission intensity is lower by a factor of around 12 compared to the TMGqu emission, showing another case of Cu^{II} quenching the fluorescence emission as expected.[45, 65] The TMGqu ligand itself shows an emission spectrum with a maximum at around 510 nm with again the same broadening on the right side which is expected as the fluorescence most likely originates from the aromatic rings in the ligand.

When taking a quick glance at the shape of the decay curves in figure 4.14(b), one can clearly see the slower decay times of the Cu^{II} complex compared to the Cu^I complex. On first impression this may seem surprising as one might expect the opposite result for a quenched fluorescence process. It will be shown later that the decay constants of the Cu^{II} is more comparable to those of the pure ligand, whereas the Cu^I oxidation state provides access to different decay processes.



Figure 4.14: a) Steady state spectra of the TMGqu ligand (intensity devided by 3.5), the Cu^I (intensity devided by 1.5) and the Cu^{II} (intensity multiplied by 4) complex at 410 nm incident photon energy and b) Time-resolved fluorescence of TMGquCu^I (dark green), TMGquCu^{II} (light green) and the TMGqu ligand (blue) at 410 nm incident photon energy and 510 nm emission wavelength. The IRF is shown for completeness.

TMGqu

Figure 4.15 shows the emission spectra of the TMGqu ligand. While the shapes are roughly the same for all incident photon energies, with again the same broadening on the right side. The maxima of the emission shift to higher wavelengths from around 510 nm for 366 nm and to 520 nm for 410 nm. Also the intensities follow the decreasing absorption for higher wavelengths as can be seen in figure 4.11(a).



Figure 4.15: Fluorescence emission spectra of the TMGqu ligand for different incident photon energies normalized to the incident laser power. The maximum of the emission is at around 510 nm with again the same broadening on the right side. There is also a slight shift to higher wavelengths for lower incident photon energies. Shown as vertical lines are the selected fluorescence emission wavelengths 450 nm, 470 nm, 490 nm, 510 nm, 530 nm and 550 nm.

Table 4.6 provides an overview of the decay lifetimes for different concentrations and incident photon energies for the TMGqu ligand. The chronological order of the measurements was 410 nm, 390 nm, 375 nm and finally the 366 nm one.

The decay process consists of three components for both measured concentrations. For 0.01 mM, the slowest decay is around 7.5 ns to 10.5 ns at 366 nm incident photon energy, changing with incident photon energies and emission wavelengths to slower decays between 11.2 ns and 15.8 ns at 410 nm incident photon energy. The slower component is more stable and only changes slightly with the emission wavelength. It also shows the same behavior for different incident photon energies and changes from around 2.6 ns for 366 nm incident photon energy to 3.2 ns at 411 nm. The fast component demonstrates greater noise but also shows a slight increase for lower incident photon energies growing from around 180 ps at 366 nm to 205 ps at 410 nm. What can be seen as well is higher noise levels for higher emission wavelengths. This leads to longer integration times and thus higher noise in the decay spectrum.

The same behavior is also seen for all other concentrations and it seems no collisional quenching effects influence the sample. Additional effects are observed in the 0.1 mM sample after the measurement at 410 nm since the effect of the faster decay components that one might relate to collisional quenching disappears at the higher 1 mM sample negating quenching effects.

The presence of three decay times is an indicator that several electronical states are reached from the excited state and at least three decay radiatively. Which states and what processes are involved is not part of this work and should be investigated later on by a detailed study and accompanying calculations.



Figure 4.16: *TMGqu fluorescence emission spectrum at a)* 366 nm and b) 410 nm incident photon energy with fit and respective fit components.

Table 4.6: Fluorescence decay times for the TMGqu ligand for different incident photon energies and different emission wavelengths. The fluorescence consists of
three separate decay components where the slowest changes its behavior depending on the emission wavelength from around 8 ns to around 16 ns. The
faster component is roughly 2.8 ns and does not seem to be dependent on the emission wavelength. The fast component is around 190 ps. Also it seems
that compared to the copper complexes of TMGqu effects of collisional quenching are small even for 1 mM solutions as no changes in the decay times can
be observed. The 0.1 mM solution seems to have changed after the 410 nm measurement, as decay times only changed for those samples.

wl_i	wl_{fluo} [nm]	$ au_1$	$ au_2$	$oldsymbol{ au_3} [ext{ns}]$	$ au_1$	$ au_2$	$oldsymbol{ au_3} [\mathrm{ns}]$	$ au_1$	$ au_2$	$oldsymbol{ au_3} [\mathrm{ns}]$
			0.01 mM			0.1 mM			1 mM	
	450	7.3 ± 0.17	2.5 ± 0.02	0.231 ± 0.04	6.3 ± 0.06	2.4 ± 0.02	0.219 ± 0.04	9.8 ± 0.09	2.9 ± 0.03	0.222 ± 0.03
	470	7.9 ± 0.10	2.6 ± 0.02	0.203 ± 0.02	6.3 ± 0.08	2.4 ± 0.02	0.206 ± 0.02	10.0 ± 0.12	2.9 ± 0.02	0.189 ± 0.02
366	490	8.7 ± 0.15	2.6 ± 0.02	0.193 ± 0.02	6.1 ± 0.09	2.4 ± 0.02	0.180 ± 0.01	10.5 ± 0.16	2.9 ± 0.02	0.181 ± 0.02
	510	9.8 ± 0.19	2.6 ± 0.02	0.179 ± 0.01	6.2 ± 0.11	2.5 ± 0.02	0.178 ± 0.01	10.7 ± 0.16	2.8 ± 0.02	0.169 ± 0.02
	530	10.8 ± 0.24	2.6 ± 0.03	0.179 ± 0.01	6.2 ± 0.17	2.5 ± 0.02	0.172 ± 0.01	11.3 ± 0.20	2.9 ± 0.02	0.191 ± 0.01
	550	11.2 ± 0.25	2.6 ± 0.03	0.174 ± 0.01	6.3 ± 0.18	2.5 ± 0.02	0.170 ± 0.01	12.0 ± 0.31	2.9 ± 0.03	0.167 ± 0.01
	450	7.9 ± 0.07	2.6 ± 0.03	0.234 ± 0.04	6.4 ± 0.06	2.4 ± 0.02	0.207 ± 0.03	9.9 ± 0.09	2.9 ± 0.03	0.214 ± 0.04
	470	8.5 ± 0.10	2.7 ± 0.02	0.199 ± 0.03	6.3 ± 0.07	2.5 ± 0.02	0.199 ± 0.02	10.1 ± 0.12	2.9 ± 0.03	0.196 ± 0.03
275	490	9.6 ± 0.15	2.7 ± 0.02	0.194 ± 0.02	6.2 ± 0.09	2.4 ± 0.02	0.179 ± 0.01	10.6 ± 0.17	2.9 ± 0.03	0.184 ± 0.02
375	510	10.7 ± 0.19	2.7 ± 0.03	0.203 ± 0.01	6.3 ± 0.11	2.5 ± 0.02	0.187 ± 0.01	11.0 ± 0.21	2.9 ± 0.03	0.208 ± 0.01
	530	11.3 ± 0.22	2.7 ± 0.03	0.190 ± 0.01	6.2 ± 0.15	2.5 ± 0.02	0.197 ± 0.01	11.6 ± 0.27	2.9 ± 0.03	0.182 ± 0.01
	550	12.1 ± 0.26	2.7 ± 0.03	0.208 ± 0.01	5.9 ± 0.16	2.5 ± 0.02	0.180 ± 0.01	12.3 ± 0.32	2.9 ± 0.03	0.192 ± 0.01
	450	8.6 ± 0.08	2.7 ± 0.03	0.301 ± 0.05	6.8 ± 0.06	2.4 ± 0.02	0.391 ± 0.05	10.0 ± 0.09	2.9 ± 0.03	0.299 ± 0.06
	470	9.7 ± 0.12	2.8 ± 0.03	0.262 ± 0.03	6.8 ± 0.07	2.4 ± 0.02	0.208 ± 0.02	10.5 ± 0.13	2.9 ± 0.03	0.242 ± 0.03
200	490	11.1 ± 0.17	2.8 ± 0.03	0.219 ± 0.02	6.7 ± 0.10	2.4 ± 0.02	0.209 ± 0.01	11.3 ± 0.19	2.9 ± 0.03	0.217 ± 0.02
390	510	12.4 ± 0.22	2.8 ± 0.03	0.207 ± 0.01	6.6 ± 0.12	2.4 ± 0.02	0.199 ± 0.01	12.1 ± 0.24	2.9 ± 0.03	0.234 ± 0.01
	530	13.2 ± 0.25	2.9 ± 0.04	0.205 ± 0.01	6.7 ± 0.15	2.4 ± 0.02	0.199 ± 0.01	13.0 ± 0.31	2.9 ± 0.03	0.227 ± 0.01
	550	13.7 ± 0.25	2.9 ± 0.04	0.199 ± 0.01	6.8 ± 0.20	2.5 ± 0.02	0.196 ± 0.01	13.8 ± 0.41	2.9 ± 0.04	0.198 ± 0.01
	450	10.5 ± 0.21	2.9 ± 0.06	0.282 ± 0.07	10.0 ± 0.11	2.9 ± 0.04	0.196 ± 0.03	10.6 ± 0.11	2.9 ± 0.03	0.214 ± 0.03
	470	11.5 ± 0.23	2.9 ± 0.05	0.173 ± 0.02	10.3 ± 0.14	2.9 ± 0.03	0.204 ± 0.01	11.7 ± 0.16	3.0 ± 0.03	0.229 ± 0.02
410	490	14.0 ± 0.22	3.1 ± 0.04	0.210 ± 0.01	10.9 ± 0.19	2.9 ± 0.03	0.205 ± 0.01	13.2 ± 0.24	3.0 ± 0.04	0.214 ± 0.01
410	510	14.7 ± 0.25	3.1 ± 0.04	0.205 ± 0.01	11.2 ± 0.27	2.9 ± 0.04	0.193 ± 0.01	14.5 ± 0.35	3.0 ± 0.04	0.198 ± 0.01
	530	15.5 ± 0.31	3.2 ± 0.05	0.271 ± 0.01	11.3 ± 0.32	2.9 ± 0.04	0.192 ± 0.01	15.4 ± 0.40	3.0 ± 0.05	0.210 ± 0.01
	550	15.8 ± 0.33	3.2 ± 0.06	0.197 ± 0.01	12.7 ± 0.40	3.0 ± 0.04	0.203 ± 0.01	16.0 ± 0.46	3.0 ± 0.05	0.193 ± 0.01

63
Judging from the results it appears that there are several stable excitable states in the ligand around an energy between 2,4 eV and 2.45 eV. When analyzing the components for different emission wavelengths (see figure 4.16), the fluorescence seems to be made up of three main contributors: a slower component at 505 nm, a faster component at 547 nm and an even faster component at 593 nm. From their intensities, it is also clear that the slower processes dominate the "left" side of the spectrum while the faster components the "right" side.

As shown in table 4.7, the amplitudes of the three components also show this behavior as the slower two components lose intensity for higher emission wavelength, giving rise to the fast component. Amplitudes are only shown for the lowest and highest incident photon energies 410 nm and 366 nm as the behavior does not change with the energy. The amplitudes for the slow component have a confidence interval of $<\pm 4$, for the faster one $<\pm 13$, and for the fastest one $<\pm 55$ so the trends of the amplitudes are real.

The fit of the steady state spectrum also shows a shift to lower energies for lower incident photon energies, as for the 410 nm excitation, the faster components are shifted to the right. The spectral weight of the fit is also shifted to the right side with faster components. This is however not reflected in the amplitudes. It should be clear that the fit can only be an approximation as there are probably more components with lower spectral weight which cannot be detected with the current setup.

$\boldsymbol{wl_i} \; [\mathrm{nm}]$	wl_{fluo} [nm]	A_{τ_1}	$\mathbf{A}_{\boldsymbol{\tau_2}}$	A_{τ_3}	A_{τ_1}	$\mathbf{A}_{\boldsymbol{\tau_2}}$	A_{τ_3}	A_{τ_1}	$\mathbf{A}_{\boldsymbol{\tau_2}}$	A_{τ_3}
	0.01 mM				$0.1\mathrm{mM}$			1 mM		
								_		
	450	211	1151	541	215	1154	450	202	1149	431
	470	119	1149	723	138	1123	789	119	1124	738
266	490	77	1055	1036	95	1027	1005	72	1040	1075
200	510	47	912	1251	59	897	1306	46	892	1309
	530	34	791	1401	42	773	1707	32	779	1438
	550	33	691	1704	29	679	1742	23	684	1949
	450	69	428	203	189	905	702	170	931	648
	470	41	324	501	91	704	932	86	791	990
410	490	60	646	1232	51	604	1369	44	611	1527
410	510	47	497	1518	29	451	1690	26	447	1693
	530	38	389	1818	17	340	1984	20	349	1874
	550	35	336	1848	14	273	2021	17	281	1936

 Table 4.7: Fluorescence decay times amplitues for the TMGqu ligand for different incident photon energies and different emission wavelengths.

TMGquCu^{II}

Looking at the steady-state spectra of the TMGquCu^{II} complex in figure 4.17, the components of the fluorescence can be observed more prominently than for the previous steady-state spectra of the ligand and the Cu^{I} complex.



Figure 4.17: Fluorescence emission spectra of TMGquCu^{II} for different incident photon energies normalized to the incident laser power. The maximum of the Cu^{II} spectrum is slightly shifted to the right compared to the TMGquCu^I complex. There is also a dependence on the incident photon energy. For 366 nm the, maximum is around 530 nm which shifts to the right to 560 nm for 410 nm. Furthermore, the broadening on the right side which could be seen for the Cu^I complex makes an appearance as a distinct peak at around 620 nm. Compared to the intensity of the fluorescence of the TMGquCu^I complex, it appears that the main peak becomes heavily quenched. Shown as vertical lines are the selected fluorescence emission wavelengths 450 nm, 470 nm, 490 nm, 510 nm, 530 nm and 550 nm.

Table 4.9 provides an overview of the decay lifetimes for different concentrations and incident photon energies for the TMGquCu^{II} complex. The decay process consists of only two components for all measured concentrations. For 0.01 mM, the slowest component is around ≈ 19 ns to 21 ns at 366 nm incident photon energy (excluding the Raman peaks), changing with the incident photon energies and emission wavelengths to faster decays between 12 ns and 14 ns at 410 nm incident photon energy. The slower component shows the trend which could already be observed for the ligand and changes considerably with the emission wavelength from around 2 ns at 450 nm to around 8 ns for 550 nm. The amplitudes for the slow component have a confidence interval of $<\pm 19$ and $<\pm 14$ for the faster one. As the confidence ranges are smaller than the increase in decay time this trend is not an artifact coming from the fit but a real physical property of the sample. The errors for both components follows the trend of the amplitude nicely. As the amplitude of the slower decay channel increases for increasing emission wavelengths, the error decreases as expected. The error increases for the faster component as the amplitude decreases and the error decreases again as the amplitude increases nearing the 550 nm emission wavelength.

The fit shows that for Cu^{II} there are only two components necessary to get a good representation of the spectrum. This could either be an indicator that one of the two slower components in the Cu^I complex has been completely quenched, or that another decay channel has been opened



Figure 4.18: *TMGquCu^{II}* fluorescence emission spectrum at a) 366 nm and b) 410 nm incident photon energy with fit and respective fit components.

by the Cu^{II}. Further analysis on this is still needed and should be part of future experimental research. Also the shift to lower energies can be observed in the fit (527 nm to 555 nm and 598 nm to 649 nm). For 410 nm incident photon energy the width for the two Gaussian fits have changed sides and the broader faster component is now on the higher energy "left" side. This explains why for lower incident photon energies the decay times become faster for the slower component. One would expect from the fit that for an energy in between the used wavelengths, the decay times of the emission wavelength-dependent component would change its trend from slow to fast to fast to slow, but this is not observed not happen and should be further investigated in the future.

$\boldsymbol{wl_i} \; [ext{nm}]$	wl_{fluo} [nm]	A_{τ_1}	$\mathbf{A}_{\boldsymbol{\tau_2}}$	A_{τ}	A_{τ_2}	A_{τ_1}	A_{τ_2}
		0.01 mM			0.1 mM	1 mM	
	450	78	450	22	394	13	248
	470	315	427	34	309	22	189
266	490	694	365	79	256	44	146
300	510	965	318	152	2 218	83	133
	530	932	328	244	4 232	126	131
	550	1035	407	312	2 292	160	162
	450	-	-	-	-	-	-
	470	-	-	-	-	-	-
410	490	308	166	54	47	33	26
410	510	934	470	121	L 77	63	39
	530	-	-	176	6 128	87	69
	550	340	365	183	3 252	111	150

Table 4.8: Fluorescence decay times amplitudes for the TMGquCu^{II} complex for different incident photon energies and different emission wavelengths.

When looking at the amplitudes (see table 4.8), both components show a rise for the first component for all concentrations, as well as a dip-like behavior for the second component.

The changing decay times and the changing amplitudes are again an indicator that there are

probably more than two decay constants involved which cannot be accessed with the current setup. The Cu^{II} in the complex seems to open up a non-radiative decay channel which would explain the much reduced intensity. The remaining fluorescence originates from the ligand when looking at the decay times behavior.

Table 4.9: Fluorescence decay times for the $TMGquCu^{II}$ complex for different incident photon energies and different emission wavelengths. The fluorescence consists of two separate decay components compared to the three of the $TMGquCu^{I}$ complex. For the 0.01 mM solution, the slower component is in the range of roughly 15.5 ns when excluding the 366 nm and 410 nm measurement where impurities showed in the steady state spectrum. The faster component shows an interesting behavior as it appears to be emission wavelength dependent. Starting at circa 2 ns at 450 nm emission going up to nearly 8 ns at 500 nm emission. Also as for the $TMGquCu^{I}$ complex for higher concentrations can be observed. Quenching effects appear to already reach a maximum at 0.1 mM since for 1 mM no further changes can be observed in the decay times. Signal level was too low for several wavelengths, those are marked with "-".

$\boldsymbol{wl_i} \; [\mathrm{nm}]$	wl_{fluo} [nm]	$ au_1$	$ au_2$	$ au_1$	$ au_2$	$ au_1$	$ au_2$	
		0.01	mM	0.1 n	nM	1 mM		
	450	17.3 ± 0.37	1.8 ± 0.08	7.2 ± 0.35	1.5 ± 0.04	7.8 ± 0.48	1.6 ± 0.05	
	470	17.8 ± 0.18	1.9 ± 0.13	11.0 ± 0.36	1.6 ± 0.06	11.1 ± 0.41	1.6 ± 0.07	
200	490	18.7 ± 0.12	2.6 ± 0.23	11.5 ± 0.22	1.6 ± 0.08	11.5 ± 0.28	1.6 ± 0.10	
366	510	19.4 ± 0.10	5.4 ± 0.34	11.5 ± 0.16	1.8 ± 0.12	11.2 ± 0.21	1.6 ± 0.14	
	530	19.9 ± 0.11	6.8 ± 0.38	11.6 ± 0.14	2.3 ± 0.17	11.0 ± 0.17	1.9 ± 0.18	
	550	21.0 ± 0.09	8.3 ± 0.33	12.4 ± 0.13	3.5 ± 0.18	11.4 ± 0.19	2.6 ± 0.19	
	450	15.9 ± 0.23	1.7 ± 0.12	9.8 ± 0.42	1.4 ± 0.05	7.3 ± 0.48	1.5 ± 0.09	
	470	15.9 ± 0.11	1.8 ± 0.17	12.3 ± 0.30	1.4 ± 0.09	10.8 ± 0.40	1.5 ± 0.13	
275	490	15.6 ± 0.09	2.6 ± 0.30	12.5 ± 0.22	1.6 ± 0.16	11.7 ± 0.30	1.5 ± 0.21	
375	510	15.6 ± 0.11	6.1 ± 0.37	12.9 ± 0.16	2.0 ± 0.23	12.0 ± 0.22	2.1 ± 0.31	
	530	15.5 ± 0.08	6.6 ± 0.37	12.2 ± 0.13	3.1 ± 0.27	12.3 ± 0.19	2.7 ± 0.32	
	550	15.5 ± 0.08	7.6 ± 0.31	12.8 ± 0.14	4.8 ± 0.20	12.6 ± 0.19	3.4 ± 0.28	
	450	15.9 ± 0.34	1.7 ± 0.12	10.4 ± 0.58	1.4 ± 0.09	-	-	
	470	-	-	14.4 ± 0.51	1.5 ± 0.16	13.3 ± 0.30	1.1 ± 0.39	
200	490	-	-	13.4 ± 0.29	1.6 ± 0.21	12.3 ± 0.21	1.5 ± 0.57	
390	510	15.8 ± 0.10	3.7 ± 0.26	14.8 ± 0.25	2.4 ± 0.29	12.1 ± 0.17	1.9 ± 0.55	
	530	-	-	14.8 ± 0.21	2.8 ± 0.27	12.2 ± 0.15	3.0 ± 0.49	
	550	14.3 ± 0.08	4.9 ± 0.22	15.5 ± 0.21	3.8 ± 0.23	12.6 ± 0.16	3.6 ± 0.33	
	450	-	-	-	-	-	-	
410	470	-	-	-	-	-	-	
	490	12.7 ± 0.12	3.6 ± 0.33	11.1 ± 0.22	1.4 ± 0.23	11.3 ± 0.25	1.3 ± 0.28	
	510	12.7 ± 0.08	2.9 ± 0.18	11.1 ± 0.16	2.0 ± 0.26	10.8 ± 0.19	2.0 ± 0.32	
	530	-	-	11.6 ± 0.15	3.0 ± 0.24	11.1 ± 0.17	3.0 ± 0.27	
	550	12.9 ± 0.16	3.8 ± 0.28	13.1 ± 0.26	4.1 ± 0.24	11.6 ± 0.19	3.4 ± 0.19	

TMGquCu^I

Figure 4.19 shows the emission spectra of the TMGquCu^I complex for different incident photon energies. The spectra show a maximum at around 520 nm and an almost symmetric profile with a slight broadening on the right side. The 390 nm and 410 nm spectra are slightly shifted to the left and right which may be caused by impurities in the glassware while dissolving the complex. Again the investigated emission wavelengths are shown.



Figure 4.19: Fluorescence emission spectra of TMGquCu^I for different incident photon energies normalized to the incident laser power. The spectra show a maximum at around 520 nm and an almost symmetrical profile with a slight broadening on the right side. The 390 nm and 410 nm spectra are slightly shifted to the left and right which may be caused by impurities in the glassware while dissolving the complex. Also shown are the selected fluorescence emission wavelengths 450 nm, 470 nm, 490 nm, 510 nm, 530 nm and 550 nm.

Table 4.12 provides an overview of the decay lifetimes for different concentrations and incident photon energies for the TMGquCu^I complex. The decay process consists of three components for both measured concentrations. For 0.1 mM, the slowest component is around roughly 8.2 ns, the faster component around 2.6 ns, and the fastest process in the range of around 190 ns. It is easy to see that the decay times do not change with the incident photon energy. This is supported by Kasha's rule which states that molecules in the electronic excited state quickly relax to their lowest states $(10^{-13} \text{ s to } 10^{-211} \text{ s})$ where fluorescence is then emitted from.[42] Another interesting aspect of the TMGquCu^I complex is that decay times also do not change for different emission wavelengths. This supports the idea that there are only those three decay channels involved for the fluorescence of the complex. Going to higher concentrations, collisional quenching effects can be seen.

No definitive trend can be seen in the steady state spectra, but as with the ligand, there are multiple excitable states in the TMGquCu^I complex (albeit the energy spread is smaller than for TMGqu alone). When analyzing the components for different emission wavelengths the fluorescence is made up of three contributors which is also supported by the fit (see figure 4.16). From the fit the first two components at 505 nm and 547 nm have almost identical FWHM, therefore the decay times are roughly identical and dominate the slower left side of the spectrum. At 593 nm there is a broader third component which amounts to a faster decay channel on the



"right" side of the spectrum where it shows the asymmetrical broadening.

Figure 4.20: $TMGquCu^{I}$ fluorescence emission spectrum at a) 366 nm and b) 410 nm incident photon energy with fit and respective fit components.

For lower incident photon energies, the two right components move to lower energies (547 nm to 552 nm and 593 nm to 600 nm). As within the TMGqu ligand, the faster component increases its spectral weight thus leading to slightly faster decay times for higher emission wavelengths. This is also supported by the amplitudes for the three components as shown in table 4.10. While the amplitudes (see table 4.10) for the two slower components decrease for higher emission wavelengths, the fast component rises quickly. The amplitudes for the slow component have a confidence interval of $<\pm 4$, the faster one $<\pm 11$, and the fastest one $<\pm 50$ so the trends of the amplitudes are real.

As with the steady state fit for the TMGqu ligand, it should also be kept in mind that the fit is only an approximation and more components currently not detectable with the setup could be present. This should be the focus of research when detector hardware improves.

wl_i [nm]	wl_{fluo} [nm]	A_{τ_1}	A_{τ_2}	A_{τ_3}	A_{τ_1}	$\mathbf{A}_{\boldsymbol{\tau_2}}$	$\mathbf{A}_{\boldsymbol{\tau_3}}$
			0.1 mM			1 mM	
	150	~					
	450	61	1310	281	227	1104	280
	470	44	1240	461	147	1165	473
266	490	25	(2084)	714	100	1014	681
300	510	20	955	948	70	907	1006
	530	19	822	1315	60	701	1180
	550	10	707	1359	40	675	1329
	450	-	-	-	-	-	-
	470	-	-	-	-	-	-
410	490	-	-	-	-	-	-
410	510	19	370	1360	36	278	1108
	530	20	293	1625	32	240	1600
	550	29	259	1746	23	250	1746

Table 4.10: Fluorescence decay times amplitues for the $TMGquCu^I$ complex for different incident photon
energies and different emission wavelengths.

Resuming dicussions on the decay constants of the X-ray measurements, the values of the time-resolved fluorescence measurements fit in reasonaby well when looking at the bigger $\Delta \tau$ values for the XAFS measurements. Collisional quenching effects can be observed in both experiments and are on a consistent time scale (see table 4.11), making both results complementary and confirming the measured time scales. One should also keep in mind that the XAFS decay times are averaged over the whole emission which will certainly give slightly different decay constants than those from a single emission wavelenght.

Table 4.11: Decay time comparisons between time-resolved fluorescence (366 nm incident photon energy and 510 nm emission wavelength, F) and time-resolved XAFS (X) data shows good agreement within the error range. Also it seems XAFS is unable to see the third decay which might be within the noise.

	F $0.1\mathrm{mM}$	F $1.0\mathrm{mM}$	X $1.0\mathrm{mM}$	X $2.0\mathrm{mM}$	X 5.0 mM
$\begin{array}{c} \tau_1 \\ \Delta \tau_1 \end{array}$	$\begin{array}{c} 192\mathrm{ps}\\ 10\mathrm{ps} \end{array}$	$\frac{184\mathrm{ps}}{20\mathrm{ps}}$	$130\mathrm{ps}$ $35\mathrm{ps}$	$\frac{124\mathrm{ns}}{20\mathrm{ps}}$	$\frac{106\mathrm{ps}}{20\mathrm{ps}}$
$\tau_2 \\ \Delta \tau_2$	$\begin{array}{c} 8.0\mathrm{ns}\\ 0.25\mathrm{ns} \end{array}$	$\begin{array}{c} 4.7\mathrm{ns}\\ 0.08\mathrm{ns} \end{array}$	$6.3\mathrm{ns}$ $2.5\mathrm{ns}$	$\begin{array}{c} (7.9\mathrm{ns})\\ (6.5\mathrm{ns}) \end{array}$	$3.4\mathrm{ns}$ $2.1\mathrm{ns}$
$\tau_3 \\ \Delta \tau_3$	$\begin{array}{c} 2.6\mathrm{ns}\\ 0.02\mathrm{ns} \end{array}$	$\begin{array}{c} 2.0\mathrm{ns}\\ 0.02\mathrm{ns} \end{array}$			

As with other copper complexes, multiple decay times are an indicator that multiple energetic levels between the excited state and the ground state are involved in the decay process.[9, 38, 52, 71] S. Herres-Pawlis and Wolfgang Zinth (personal communications, 17.12.2015) suggest based on data from time-resolved ultraviolet–visible spectroscopy (UV-Vis) and transient infrared spectroscopy that the wavelength-dependent excited state S_n decays within 0.2 ps to 0.3 ps to the S₁ state. S_n shows slight Cu^{2+} character while the ground state is Cu^+ as expected. S₁ has two decay channels. One is to a "hot ground state" within 1.3 ps which vibrationally cools within 11 ps to the ground state. 50% of the population follows this path. The other half decays to a T₁ triplet state which decays within 120 ps to the "cool" ground state. 95% of the triplet state population follows this path which can be seen both in the time-resolved XAFS data as well as in the time-resolved fluorescence data within the error margin. The remaining 5% follow slower decay paths via other lower energetic states. Time-resolved XAFS data shows one decay path whereas time-resolved fluorescence shows two decay paths. (To be published, see Appendix B5.) Further measurements on this part of the population of the T₁ triplet state are indispensable and more measurements should be conducted in the future.

Table 4.12: Fluorescence decay times for the TMGquCu^I complex for different incident photon energies and different emission wavelengths. The fluorescence consists
of three separate decay components. A slower one at roughly 8 ns, a faster one at around 2.6 ns and a fast one at about 190 ps for the 0.01 mM solution.
Also quenching at higher concentrations can be observed as for the 1 mM solution the slow component goes down from 8 ns to roughly 4.8 ns, the faster
one from 2.6 ns to 2 ns. The fast component changes from around 190 ps to 180 ps. Signal level was too low for several wavelengths, those are marked
with "-".

$\boldsymbol{wl_i} \; [ext{nm}]$	wl_{fluo} [nm]	$ au_1$	$ au_2$	$oldsymbol{ au_3} [\mathrm{ns}]$	$ au_1$	$ au_2$	$ au_{3} [m ns]$
			0.1 mM			1 mM	
	450	8.4 ± 0.14	2.5 ± 0.02	0.258 ± 0.06	4.9 ± 0.05	2.0 ± 0.02	0.299 ± 0.07
	470	8.3 ± 0.17	2.6 ± 0.02	0.180 ± 0.03	4.9 ± 0.06	2.0 ± 0.02	0.192 ± 0.03
966	490	8.4 ± 0.25	2.6 ± 0.02	0.187 ± 0.01	4.8 ± 0.07	2.0 ± 0.01	0.204 ± 0.02
300	510	8.0 ± 0.25	2.6 ± 0.02	0.192 ± 0.01	4.7 ± 0.08	2.0 ± 0.01	0.184 ± 0.02
	530	(7.1 ± 0.25)	2.6 ± 0.02	0.194 ± 0.01	4.6 ± 0.09	2.0 ± 0.01	0.182 ± 0.01
	550	8.3 ± 0.40	2.6 ± 0.02	0.196 ± 0.01	4.9 ± 0.09	2.0 ± 0.02	0.184 ± 0.01
	450	8.0 ± 0.14	2.6 ± 0.02	0.302 ± 0.08	4.6 ± 0.05	2.0 ± 0.02	0.227 ± 0.04
	470	8.5 ± 0.17	2.7 ± 0.02	0.190 ± 0.03	4.6 ± 0.06	2.0 ± 0.01	0.186 ± 0.02
275	490	8.3 ± 0.22	2.7 ± 0.02	0.199 ± 0.02	4.7 ± 0.08	2.1 ± 0.01	0.212 ± 0.01
919	510	8.3 ± 0.27	2.7 ± 0.02	0.203 ± 0.01	4.7 ± 0.10	2.1 ± 0.01	0.220 ± 0.01
	530	8.0 ± 0.31	2.7 ± 0.02	0.186 ± 0.01	4.5 ± 0.11	2.0 ± 0.02	0.182 ± 0.01
	550	8.0 ± 0.30	2.7 ± 0.02	0.217 ± 0.01	4.2 ± 0.13	2.0 ± 0.02	0.188 ± 0.01
	450	8.1 ± 0.14	2.6 ± 0.02	0.252 ± 0.06	4.9 ± 0.06	1.9 ± 0.02	0.165 ± 0.03
	470	8.2 ± 0.16	2.6 ± 0.02	0.212 ± 0.02	4.9 ± 0.06	1.9 ± 0.02	0.168 ± 0.02
200	490	7.9 ± 0.18	2.6 ± 0.02	0.220 ± 0.01	5.3 ± 0.08	2.0 ± 0.02	0.210 ± 0.01
390	510	7.7 ± 0.21	2.6 ± 0.02	0.186 ± 0.01	5.3 ± 0.09	2.0 ± 0.02	0.204 ± 0.01
	530	7.9 ± 0.25	2.6 ± 0.02	0.182 ± 0.01	5.4 ± 0.11	2.0 ± 0.02	0.184 ± 0.01
	550	7.6 ± 0.27	2.5 ± 0.02	0.178 ± 0.01	5.7 ± 0.13	2.0 ± 0.02	0.182 ± 0.01
	450	-	-	-	-	-	-
410	470	-	-	-	-	-	-
	490	-	-	-	-	-	-
	510	8.0 ± 0.03	2.7 ± 0.03	0.192 ± 0.01	5.4 ± 0.12	2.0 ± 0.03	0.180 ± 0.01
	530	8.0 ± 0.03	2.7 ± 0.03	0.188 ± 0.01	5.6 ± 0.13	2.0 ± 0.03	0.178 ± 0.01
	550	7.9 ± 0.03	2.7 ± 0.05	0.189 ± 0.01	5.8 ± 0.17	2.0 ± 0.04	0.180 ± 0.01

72

Chapter 5

Summary and Outlook

This work has characterized modern copper based complexes by using multiple state of the art spectroscopic methods. With Raman spectroscopy it was shown that TMGquCu^I in its so called entatic state, a twisted molecule structure which puts its geometric properties between tetrahedral and square- planar configuration, should be optically triggerable to become a Cu^{II} complex at a resonance energy of around 3.4 eV. Further results from the resonance Raman study show that the counter ions PF₆ or TfO do not change the Raman spectrum. Solvents however, due to their steric and polar influence, do change the behavior of the complex.

X-ray absorption spectroscopy has shown that the Cu^{II} can indeed be triggered upon optical excitation. The TMGquCu^I excited state absorption spectrum almost overlaps the TMGquCu^{II} ground state spectrum. While theory predicts this is also possible in the reverse direction, it has not been possible to show this kind of behavior yet. With improved detector accuracy and faster detection methods, it might become possible to measure in the future.

Using time-resolved fluorescence spectroscopy, the time constants of the decay processes have been investigated for several incident photon energies and emission wavelengths. All steady state spectra are mainly influenced by the TMGqu ligand (as one would expect), however the different oxidation states of the copper have completely different effects on the fluorescence. While the Cu^I complex does not show any influence of either different excitation energies or emission wavelengths, the Cu^{II} complex shows much slower decay times and a much decreased fluorescence intensity. This is caused by Cu^{II} being a well-known fluorescence quencher. Furthermore the decay times on the remaining Cu^{II} fluorescence resembles the behavior from the TMGqu ligand. Interestingly the Cu^{II} seems to only quench the fluorescence intensity and the decay times in the Cu^{II} complexes become slower compared to the Cu^I. Moreover, the time constants for the Cu^I are consistent between both time-resolved methods used for this work. Collisional quenching effects can be observed for both complexes, but not for the ligand only, where the concentrations are still too low to observe any effects of quenching.

The current setups used in this thesis offer great possibilities for steady-state measurements and time-resolved studies beginning at 25 ps after the excitation. First time-resolved Raman measurements show that most of the vibrational processes have already decayed after those 25 ps, demonstrating that time-resolved Raman spectroscopy is a crucial method to fully understand the processes involved that requires further measurements on the complexes to be conducted. In addition, further measurements on how different solvents interact with the complexes are needed, as well as theoretical models describing those interactions. As all of the above measurements are currently prone to sample degradation due to the high laser power needed, methods for minimizing radiation damage should be applied. This can be tackled in different ways. For the Raman measurements, a flow cuvette could be used which would result in the laser being always incident on fresh sample, without creating residue inside the cuvette. This cuvette must be designed to fit into the entrance optics, and Suprasil quartz glass is needed for the cuvette to be transparent for the broad wavelength range of the laser systems used. This would also be interesting for time-resolved fluorescence measurements as there are remaining unexplainable results which might be related to sample degradation.

Furthermore, a new Peltier element cooled cryo has been tested to avoid temperature-induced damage and also provide the possibility of in situ preparation of more room-temperature unstable complexes. At present, temperatures down to -60 °C can be reached. An ethanol-based cryo that will offer even lower temperatures is currently being built.

Vacuum jet chambers have been built for both the Raman measurements at the CFEL as well as for the VUV Raman experiments at FLASH. In these chambers it will be possible to always measure fresh sample and minimize the sample volume to the single molecule region. [14, 77, 5, 62, 81] First test measurements on the same complexes from this work show very promising results with higher peak intensities and lower sample volume being needed.

Chapter 6

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Appendix A

Software

MonoControl.py has been written for making it easier to use the McPherson monochromator with the TCSPC fluorescence setup. In the current version it supports basic features such as approaching a specific wavelength with the monochromator and provides a nice visual progress indication. It also features notification about Raman peaks of the solvents and warns the user about them with a colored warning in the target wavelength selection. For this to work, the user obviously also has to provide the current laser wavelength being used. To make it simple extending the software with new solvents, the new solvent and its Raman peaks in wavenumbers can simply be added to the config file. After a restart of the software it automatically lists the new solvent in the solvent drop down selection.

The software requires Python 3 and uses the PyQt framework for its GUI. Also the pyserial library is required for the communication with the monochromator controller.

Current versions of the program can be found here [30].

A.1 MonoControl.py

```
#!/usr/bin/env python
# -*- coding: utf-8 -*-
__author__ = "Benjamin Grimm-Lebsanft"
__copyright__ = "Copyright 2014-2015, Benjamin Grimm-Lebsanft,
Monochromator class copyright 2014, Arne Goos"
__license__ = "Public Domain"
__version__ = "1.1.0"
__status__ = "Production"
import sys, serial, logging, configparser, time
from PyQt4 import QtGui, QtCore
class Monochromator(object):
    #### Initialises a serial port
    def __init__(self):
        self.config = configparser.RawConfigParser()
```

```
self.config.read('mono.cfg')
    self.comport = self.config.get('Mono_settings', 'comport')
    self.current_wavelength = self.config.get('Mono_settings', '
       current_wavelength')
    self.speed = self.config.get('Mono_settings', 'speed')
    self.approach_speed = self.config.get('Mono_settings', '
       approach_speed')
    self.offset = self.config.get('Mono_settings', 'offset')
    self.nm_per_revolution = self.config.get('Mono_settings', '
       nm_per_revolution')
    self.steps_per_revolution = self.config.get('Mono_settings',
        'steps_per_revolution')
    self.calibration_offset = self.config.get('Mono_settings', '
       calibration_offset')
    self.mono = serial.Serial(self.comport, timeout=1)
      \#\#\# sends ascii commands to the serial port and pauses for
          half a second afterwards
def sendcommand(self,command):
    self.mono.flushInput()
    self.mono.flushOutput()
    print('Send command: ' + command)
    #logging.debug('Send command: ' + command)
    self.mono.write(bytearray(command + '\r\n', 'ascii'))
    time.sleep(0.5)
\#\!/\!/\!\!/\!\!/ reads ascii text from serial port + formatting
def readout(self):
    \#time.sleep(0.5)
    #self.mono.flushInput()
    a = self.mono.readlines()\#[0]. lstrip('|r|n')
    if not a == []:
        print('Readout : ' + a[0].rstrip('\r\n'))
        logging.debug('Readout : ' + a[0].rstrip('\r\n'))
        return a[0].rstrip('\r\n')
\#\#\# sets the ramp speed
def setRampspeed(self, rampspeed):
    self.sendcommand('K ' + str(rampspeed))
    \#time.sleep(3)
\# \# \# sets the initial velocity
def setInitialVelocity(self, initspeed):
```

```
self.sendcommand('I ' + str(initspeed))
\# \# # sets the velocity
def setVelocity(self,velocity):
    self.sendcommand('V ' + str(velocity))
#### checks if the Monochromator is moving (returns True of False
   )
def moving(self):
    self.sendcommand('^')
    a = self.readout()
    if not a[-2] == '0':
        return True
    else:
        return False
\#\!/\!/\!/\! checks if the connection to the controller is active
def checkfortimeout(self):
    try:
        self.sendcommand('X')
        if self.readout() == None:
            print('Timeout occured')
    except:
        print('Timeout occured')
#### checks for limit switch triggering
def checkLimitSwitches(self):
    self.sendcommand("]")
    a = self.readout()
    if a[-2] != '0':
        logging.warning("Limit Switch triggered")
        return True
    else:
        return False
#### moves grating into home position
def getHomePosition():
    self.sendcommand("A8")
    self.sendcommand("]")
    self.sendcommand("M+23000")
    self.sendcommand("]")
    self.sendcommand("@")
    self.sendcommand("-108000")
```

```
self.sendcommand("+72000")
    self.sendcommand("A24")
    self.sendcommand("F1000,0")
    self.sendcommand("A0")
#### moves to a specific wavelength
def approachWL(self, approach_wavelength):
    if str.isdigit(approach_wavelength):
        print("Wavelength to approach: " + approach_wavelength +
            " nm")
        nm_difference = float(approach_wavelength) - float(self.
           current_wavelength) + float(self.calibration_offset)
        print("Difference in nm [calibration offset of " + self.
           calibration_offset + " nm included]: " + str(
           nm_difference))
        step_difference = round(((float(nm_difference) / float(
           self.nm_per_revolution)) * float(self.
           steps_per_revolution))+ float(self.offset))
        print("Difference in steps: " + str(step_difference))
        time_needed_sec = abs(step_difference / int(self.speed))
            + abs(int(self.offset)/int(self.approach_speed))
        print("Time needed for operation: " + str(
           time_needed_sec) + " s")
        time_delay_for_progressbar = time_needed_sec / 100
        self.sendcommand("V" + str(self.speed))
        self.sendcommand(str(format(step_difference, '+')))
        self.sendcommand("V" + str(self.approach_speed))
        self.sendcommand("-" + str(self.offset))
        while True:
            Interface.approachButton.setEnabled(False)
            time.sleep(time_delay_for_progressbar)
            value = Interface.progressBar.value() + 1
            Interface.progressBar.setValue(value)
            QtGui.qApp.processEvents()
            if (value >= Interface.progressBar.maximum()):
                Interface.approachButton.setEnabled(True)
                Interface.progressBar.setValue(0)
                self.config.set('Mono_settings', '
                   current_wavelength', approach_wavelength)
                self.current_wavelength = int(
                   approach_wavelength)
                Interface.currentMonoWavelengthLabel.setText(str
                   (self.current_wavelength) + " nm")
```

```
f = open('mono.cfg',"w")
                    self.config.write(f)
                    break
        else:
            print("Input is not numeric")
            MessageBox = QtGui.QMessageBox.warning(Interface, "Error:
               ","Input is not numeric")
class Ui_Form(QtGui.QWidget):
    #### All UI elements go here
    def __init__(self, parent=None):
        QtGui.QWidget.__init__(self, parent)
        self.setWindowTitle('InputDialog')
        self.setFixedSize(300, 150)
        self.formLayout = QtGui.QFormLayout(self)
        self.currentMonoWavelengthLabel = QtGui.QLabel(self)
        self.currentMonoWavelengthLabel.setAlignment(QtCore.Qt.
           AlignRight)
        self.approachWavelengthInput = QtGui.QLineEdit(self)
        self.approachWavelengthInput.setMaxLength(3)
        self.approachWavelengthInput.setAlignment(QtCore.Qt.
           AlignRight | QtCore.Qt.AlignTrailing | QtCore.Qt.AlignVCenter
           )
        self.currentLaserWavelengthInput = QtGui.QLineEdit(self)
        self.currentLaserWavelengthInput.setAlignment(QtCore.Qt.
           AlignRight|QtCore.Qt.AlignTrailing|QtCore.Qt.AlignVCenter
           )
        self.combo = QtGui.QComboBox(self)
        for key, value in Mono1.config.items('RamanPeaksOfSolvents')
           •
            self.combo.addItem(key.title())
        self.combo.currentIndexChanged.connect(self.
           check_combo_state)
        self.combo.currentIndexChanged.emit(self.combo.currentIndex
           ())
```

```
self.approachWavelengthInput.textChanged.connect(self.
       check state)
    self.approachWavelengthInput.textChanged.emit(self.
       approachWavelengthInput.text())
    self.progressBar = QtGui.QProgressBar(self)
    self.progressBar.setProperty("value", 0)
    self.progressBar.setMaximum(101)
    self.approachButton = QtGui.QPushButton(self)
    self.approachButton.setObjectName("approachButton")
    self.approachButton.clicked.connect(lambda: Mono1.approachWL
       (self.approachWavelengthInput.text()))
    self.formLayout.addRow("Solvent:", self.combo)
    self.formLayout.addRow("Current Laser Wavelength:", self.
       currentLaserWavelengthInput)
    self.formLayout.addRow("Current Mono Wavelength:", self.
       currentMonoWavelengthLabel)
    self.formLayout.addRow("Approach Mono Wavelength:", self.
       approachWavelengthInput)
    self.formLayout.addRow(self.progressBar, self.approachButton
      )
    self.setWindowTitle("Mission control")
    self.currentMonoWavelengthLabel.setText(Mono1.
       current_wavelength + " nm")
    self.approachButton.setText("Approach")
    self.setLayout(self.formLayout)
def getWavenumber(self, laserWL, monoWL):
   wavenumber = abs((1/int(laserWL)) - (1/int(monoWL)))
       *10000000
   return int(round(wavenumber,0))
def check_combo_state(self, *args, **kwargs):
    solvent = self.combo.currentText()
    global raman_peaks_with_offset
   raman_peaks_list = Mono1.config.get('RamanPeaksOfSolvents',
       solvent)
   raman_range = Mono1.config.get('Settings', 'peak_range')
    raman_peaks = raman_peaks_list.split(",")
```

```
raman_peaks_with_offset = []
        for i in range(len(raman_peaks)):
            raman_peaks_with_offset += list(range(int(raman_peaks[i
               ])-int(raman_range), int(raman_peaks[i])+int(
               raman_range)))
    def check_state(self, *args, **kwargs):
        if self.approachWavelengthInput.text() and self.
           currentLaserWavelengthInput.text():
            wavenumbers = self.getWavenumber(self.
               currentLaserWavelengthInput.text(), self.
               approachWavelengthInput.text())
            print(wavenumbers)
            if wavenumbers in raman_peaks_with_offset:
                color = '#f6989d' \# red
            else:
                color = '#c4df9b' # green
            self.approachWavelengthInput.setStyleSheet('background-
               color: %s' % color)
if __name__ == "__main__":
    Mono1 = Monochromator()
    print("Initializing communication with Monochromator controller
       ...")
    Mono1.sendcommand(' ')
    app = QtGui.QApplication(sys.argv)
    Interface = Ui_Form()
    Interface.show()
    app.exec_()
```

A.2 Config file for MonoControl.py

The config file lists all important parameters of the software:

- current wavelength saves the currently used monochromator wavelength
- comport sets the comport the monochromator controller is connected to
- **speed** sets the rpm for the stepper motor inside the monochromator
- approach speed sets the rpm for the final wavelength approach, slower than "speed"
- offset defines the number of steps the stepper motor drives beyond the target position to always approach from the same side to avoid backlash
- calibration_offset in [nm]. Use if the target wavelength is not the expected approach wavelength. Should not be needed.
- nm per revolution sets the wavelength change per revolution of the stepper motor
- **steps_per_revolution** sets the steps per revolution of the stepper motor inside the monochromator. Needed for step calculations.
- **peak_range** defines the wavenumber range around a Raman peak for which a warning will be presented to the user
- Acetonitrile etc. defines the name of the solvent and their Raman peaks in wavenumbers

```
[Mono_settings]
current_wavelength = 460
comport = COM1
speed = 20000
approach_speed = 2000
offset = 30000
nm_per_revolution = 12.5
steps_per_revolution = 36000
calibration_offset = 0
[Settings]
peak_range = 5
[RamanPeaksOfSolvents]
Acetonitrile = 220,330,440,550,750
Dichloromethane = 220,330,440,550,660
Water = 100,200
```

A.3 Fit function creator

The Fit function creator script has been written to simplify creating complex fitting functions in Igor with multiple (>15) lorentzians. It creates a txt-file with three parts. The first part is the fit function which can directly be copied to the running Igor instance and compiled there. The second part is a series of Igor commands to plot the fitted lorentzians, solvent lorentzians and background into the graph. The third part consists of simple Igor commands to update the lorentzians once they have been added to the graph and modified by fitting differently. More lorentzians can be added to the fit function without changing the position of the old parameters in the W_coeff wave. Current versions of the code can be found in the group wiki. Basic usage:

- 1. Plot the solvent spectrum and fit the peaks using a fit function created with number_of_solvent_lorentzians = 0 and only using "normal" lorentzians
- 2. Use the gained parameters and intensities to put the intensity of the solvent peaks into intensity_solvent_peaks
- 3. Set number_of_solvent_lorentzians to the right value and add as much additional lorentzians for the sample as you need to number of additional lorentzians
- 4. Create a new fit function for solvent + sample
- 5. Use the draw code to create waves for the lorentzians (color and thickness are set automatically)

```
\#!/usr/bin/env python
\# -*- \ coding: \ utf-8 -*-
__author__ = "Benjamin Grimm-Lebsanft"
__copyright__ = "Copyright 2013-2015, Benjamin Grimm-Lebsanft"
__license__ = "Public Domain"
__version__ = "1.1.3"
__email__ = "benjamin@lebsanft.org"
__status__ = "Production"
## Edit to your needs
name_of_experiment = "P17_445nm"
window = "'winL275'"
coeff_wave = "W_coef"
name_of_independent_variable = "0"
number_of_solvent_lorentzians = 0
number_of_additional_lorentzians = 10
use_linear_background = 1 \# 0 no, 1 yes
color_background = "65280,21760,0"
color_solvent_lorentzians = "0,52224,0"
color_lorentzians = "0,0,0"
```

result = "\n return bg"

```
\# put in the intensity of the peaks from the fitted solvent spectrum
intensity_solvent_peaks = [1240.5,
                            70.634.
                            145.65]
## do not edit below here
\# the content of file_content is written to the file at the end of
   the code
file_content = ""
\# fit_function contains the fit_function for the curve fitting
   dialog in the form f(x)=a*x+b
fit_function = " f(" + name_of_independent_variable + ")=bg"
\# fit functions names contains all the lorentzians in names form e.g
   . lor1 = (I1 * O * q1) / ((O^2 - o1^2)^2 + (q1^2 * O^2))
fit_functions_names = ""
\# fit_functions_coeff contains all the lorentzians in coefficient
   form e.g. lor1 = (w[0] * O * w[2]) / ((O^2 - w[1]^2)^2 + (w[2]^2 * O^2))
fit_functions_coeff = ""
\# background_names contains the background in names form e.g. for a
   linear background: ug=y0+b*O
background_names = ""
\# background_coeff contains the background in coefficient form e.g.
   for a linear background: uq=w[48]+w[49]*O
background_coeff = ""
\#\ coeff names contains all the coefficients like //CurveFitDialog/w
   [16] = 06
coeff_names = ""
\# result contains the fit function result output
```

```
\# draw2 contains the shortcut for modifying already plotted
   lorentzians
draw2 = ""
\# duplicate contains the Igor duplicate wave command for the amount
   of necessary waves
duplicate = "Duplicate 'INSERTWAVENAME' bg,"
\# variable_names contains the Igor variables needed for the fit
   function
variable_names = "\n\n Variable bg\n"
file_content += "Function lor_" + str(number_of_solvent_lorentzians
   + number_of_additional_lorentzians) + "_" + name_of_experiment +
   "(w," + name_of_independent_variable + ") : FitFunc\n\n Wave w\n
     Variable " + name_of_independent_variable + "\n\n //
   CurveFitDialog/ These comments were created by the Curve Fitting
   dialog. Altering them will\n //CurveFitDialog/ make the function
    less convenient to work with in the Curve Fitting dialog.n //
   CurveFitDialog/ Equation:\n //CurveFitDialog/ Variable bg\n"
\# Devide between two cases for the background, one with and one
   without linear background
\# This of course changes the indexes and number of needed
   coefficients
\# solvent lorentzians only have position and width (hence the *2)
   and a combined intensity
\# while "normal" ones also have their respective intensity (hence
   the *3)
if(use_linear_background):
        number_of_coefficients = number_of_solvent_lorentzians*2+
           number_of_additional_lorentzians*3+3
        background_names += "\n //CurveFitDialog/ bg=y0+b*" +
           name_of_independent_variable
        background_coeff += " bg=w[0]+w[1]*" +
           name_of_independent_variable + "\n"
        draw += "bg=" + coeff_wave + "[0]+" + coeff_wave + "[1]*" +
           window + "\n"
```

```
draw2 += "bg=" + coeff_wave + "[0]+" + coeff_wave + "[1]*" +
    window + "\n"
```

else:

number_of_coefficients = number_of_solvent_lorentzians*2+

```
number_of_additional_lorentzians*3+2
        background_names += "\n //CurveFitDialog/ bg=y0"
        background_coeff += " bg=w[0] \setminus n"
        draw += "bg=" + coeff_wave + "[0]n"
        draw2 += "bg=" + coeff_wave + "[0]n"
draw += "AppendToGraph bg vs " + window + "\nModifyGraph rgb('bg')=(
   " + color_background + ")\nModifyGraph lsize('bg')=1.5\n"
if(use_linear_background):
        coeff_names += "\n\n //CurveFitDialog/ w[0] = y0\n //
           CurveFitDialog/ w[1] = b"
        if (number_of_solvent_lorentzians>0):
                coeff_names += "\n //CurveFitDialog/ w[2] = I1to" +
                    str(number_of_solvent_lorentzians)
        else:
                number_of_coefficients = number_of_coefficients-1
else:
        coeff_names += "\n\n //CurveFitDialog/ w[0] = y0"
        if (number_of_solvent_lorentzians>0):
                coeff_names += "\n //CurveFitDialog/ w[2] = I1to" +
                    str(number_of_solvent_lorentzians)
        else:
                number_of_coefficients = number_of_coefficients-1
for i in range(number_of_solvent_lorentzians+
   number_of_additional_lorentzians):
        pos1 = i
        pos2 = i*2+2
        pos3 = i*2+3
        if(number_of_solvent_lorentzians == 0):
                pos1s = 3*i+1
                pos2s = 3 * i + 2
                pos3s = 3*i+3
        else:
                pos1s = 3*i+2 - number_of_solvent_lorentzians
                pos2s = 3*i+3 - number_of_solvent_lorentzians
                pos3s = 3*i+4 - number_of_solvent_lorentzians
```

if(use_linear_background):

```
pos1 += 1
        pos2 += 1
        pos3 += 1
        pos1s += 1
        pos2s += 1
        pos3s += 1
file_content += " //CurveFitDialog/ Variable lor" + str(i
   +1) + " \ n"
result += "+lor" + str(i+1)
if (i<number_of_solvent_lorentzians+</pre>
   number_of_additional_lorentzians-1):
        duplicate += "lor" + str(i+1) + ","
else:
        duplicate += "lor" + str(i+1)
fit_function += "+lor" + str(i+1)
variable_names += " Variable lor" + str(i+1) + "\n"
\# the following part is only for solvent lorentzians as it
   contains the value (I_x/I_1) as well as a combined
   Intensity for all
if (i<number_of_solvent_lorentzians):</pre>
        fit_functions_coeff += " lor" + str(i+1) + "=(w
           [2]*(" + str(intensity_solvent_peaks[i]) +"/" +
           str(intensity_solvent_peaks[0]) + ")*" +
           name_of_independent_variable + "*w[" + str(pos3)
           + "])/((" + name_of_independent_variable + "^2-w[
           " + str(pos2) + "]^2)^2+(w[" + str(pos3) + "]^2*"
            + name_of_independent_variable +"^2))\n"
        coeff_names += "\n //CurveFitDialog/ w[" + str(pos2
           ) + "] = o" + str(pos1) + "\n //CurveFitDialog/
           w[" + str(pos3) + "] = g" + str(pos1)
        fit_functions_names += "\n //CurveFitDialog/ lor" +
            str(i+1) + "=(I1bis" + str(
           number_of_solvent_lorentzians) + "*(" + str(
           intensity_solvent_peaks[i]) +"/" + str(
           intensity_solvent_peaks[0]) + ")*" +
```

```
name_of_independent_variable + "*g" + str(pos1) +
            ")/((" + name_of_independent_variable + "^2-o" +
            str(pos1) + "^{2})^{2}+(g" + str(pos1) + "^{2}*" +
           name_of_independent_variable + "^2))"
        draw += "lor" + str(i+1) + "=(" + coeff_wave + "
           [2]*(" + str(intensity_solvent_peaks[i]) +"/" +
           str(intensity_solvent_peaks[0]) + ")*" + window +
            "*"+ coeff_wave + "[" + str(pos3) + "])/((" +
           window +"^2-" + coeff_wave + "[" + str(pos2) + "
           ]^2)^2+(" + coeff_wave + "[" + str(pos3) + "]^2*"
            + window + "^2))\nAppendToGraph " + "lor" + str(
           pos1) + " vs " + window + "\nModifyGraph rgb('" +
            "lor" + str(pos1) + "')=(" +
           color_solvent_lorentzians + ")\nModifyGraph lsize
           (" + "'lor" + str(pos1) + "')=1.5 \n''
        draw2 += "lor" + str(i+1) + "=(" + coeff_wave + "
           [2]*(" + str(intensity_solvent_peaks[i]) +"/" +
           str(intensity_solvent_peaks[0]) + ")*" + window +
            "*"+ coeff_wave + "[" + str(pos3) + "])/((" +
           window +"^2-" + coeff_wave + "[" + str(pos2) + "
           ]^2)^2+(" + coeff_wave + "[" + str(pos3) + "]^2*"
            + window + "^2))\n"
\# the following part is only for "normal" lorentzians and
   contains their respective intensity
else:
        fit_functions_coeff += " lor" + str(i+1) + "=(w[" +
            str(pos1s) + "]*" + name_of_independent_variable
            + "*w[" + str(pos3s) + "])/((" +
           name_of_independent_variable + "^2-w[" + str(
           pos2s) + "]^2)^2+(w[" + str(pos3s) + "]^2*" +
           name_of_independent_variable + "^2))\n"
        fit_functions_names += "\n //CurveFitDialog/ lor" +
            str(i+1) + "=(I" + str(pos1) + "*" +
           name_of_independent_variable + "*g" + str(pos1) +
            ")/((" + name_of_independent_variable + "^2-o" +
            str(pos1) + "^2)^2+(g" + str(pos1) + "^2*" +
           name_of_independent_variable + "^2))"
```

```
coeff_names += "\n //CurveFitDialog/ w[" + str(
                   pos1s) + "] = I" + str(pos1) + "\n //
                   CurveFitDialog/ w[" + str(pos2s) + "] = o" + str(
                   pos1) + "\n //CurveFitDialog/ w[" + str(pos3s) +
                    "] = g" + str(pos1)
                draw += "lor" + str(i+1) + "=(" + coeff_wave + "[" +
                    str(pos1s) + "]*" + window + "*" + coeff_wave +
                   "[" + str(pos3s) + "])/((" + window + "^2-" +
                   coeff_wave + "[" + str(pos2s) + "]^2)^2+(" +
                   coeff_wave + "[" + str(pos3s) + "]^2*" + window +
                    "^2))\nAppendToGraph " + "lor" + str(pos1) + "
                   vs " + window + "\nModifyGraph rgb('" + "lor" +
                   str(pos1) + "')=(" + color_lorentzians + ")\
                   nModifyGraph lsize(" + "'lor" + str(pos1) + "')
                   =1.5 n''
                draw2 += "lor" + str(i+1) + "=(" + coeff_wave + "["
                   + str(pos1s) + "]*" + window + "*" + coeff_wave +
                    "[" + str(pos3s) + "])/((" + window + "^2-" +
                   coeff_wave + "[" + str(pos2s) + "]^2)^2+(" +
                   coeff_wave + "[" + str(pos3s) + "]^2*" + window +
                    "^2))\n"
fit_function += background_names
file_content += " //CurveFitDialog/\n //CurveFitDialog/\n //
   CurveFitDialog/" + fit_function + "\n //CurveFitDialog/ End of
   Equation\n //CurveFitDialog/ Independent Variables 1\n //
   CurveFitDialog/ " + name_of_independent_variable + "\n //
   CurveFitDialog/ Coefficients " + str(number_of_coefficients)
file_content += fit_functions_names + coeff_names + variable_names +
    "\n" + background_coeff + fit_functions_coeff + result + "\nEnd
   " +"\n\" + duplicate + "\n" + draw + "\n" + draw2
\# write file to filename e.g. lor_16_360_DCM_coupled.txt
filename = "lor_" + str(number_of_solvent_lorentzians +
   number_of_additional_lorentzians) + "_" + name_of_experiment + ".
   txt"
f = open(filename, 'w+')
f.write(file_content)
f.close()
```

A.4 Powermeter.py

Due to the software supplied with the PowerMAX USB[®] missing data points or not running stable with two power meters, a new software for monitoring laser power with logging functionally has been written. Compared to the MonoControl software, special attention has been paid to making the code object oriented and the GUI threaded. The user can easily set the time interval for shown power measurements and monitor the stability over a long period of time. Logging multiple days with two power meters is no longer a problem. The latest version of the code can be found in its GitHub repository [29]

```
\#!/usr/bin/env python
\# -*- \ coding: \ utf-8 -*-
__author__ = "Benjamin Grimm-Lebsanft"
__copyright__ = "Copyright 2016, Benjamin Grimm-Lebsanft"
__license__ = "Public Domain"
__version__ = "1.2.0"
__email__ = "benjamin@lebsanft.org"
__status__ = "Production"
import serial, time, sys, random, matplotlib, decimal, logging, os
#import visa
from PyQt5.QtGui import *
from PyQt5.QtWidgets import *
from PyQt5.QtCore import *
from matplotlib.backends.backend_qt5agg import FigureCanvasQTAgg as
   FigureCanvas
from matplotlib.figure import Figure
from decimal import *
\#\#\# global data storage for later use in plots (1 day in seconds)
data1 = []
data2 = []
#rm = visa.ResourceManager('@py')
\#list of insts = rm.list resources()
### Real serial thread 1
class Worker(QObject):
    finished = pyqtSignal(float)
    def __init__(self):
        print("Serial thread init")
        super().__init__()
```

```
self.ser = serial.Serial("/dev/ttyACM0", timeout=1, xonxoff=
           True)
        \#if(len(list of insts) >= 1):
            \#self. my test inst = rm. open resource(list of insts[0])
    def work(self):
        print("Worker work")
        while(True):
            self.ser.flushInput()
            self.ser.flushOutput()
            self.ser.write(bytearray("pw?\r\n",'ascii'))
            power = self.ser.readline().decode("utf-8").lstrip().
               rstrip()
            powermW = float(power) * 1000
            #response = self.my test inst.query('READ?').split(",")
            roundedpowermW = (float("{0:.6f}".format(powermW)))
            self.finished.emit(roundedpowermW)
            time.sleep(0.1)
class Worker2(QObject):
    finished2 = pyqtSignal(float)
    def __init__(self):
        print("Serial thread init")
        super().__init__()
        self.ser = serial.Serial("/dev/ttyACM0", timeout=1, xonxoff=
           True)
    def work(self):
        print("Worker work")
        while(True):
            self.ser.flushInput()
            self.ser.flushOutput()
            self.ser.write(bytearray("pw?\r\n",'ascii'))
            power = self.ser.readline().decode("utf-8").lstrip().
               rstrip()
            powermW = float(power) * 1000
            roundedpowermW = (float("{0:.3f}".format(powermW)))
            self.finished2.emit(roundedpowermW)
```

```
### Dummy serial thread 1
class DummySerial1(QObject):
    finished = pyqtSignal(float)
    def __init__(self):
        print("Dummy serial thread 1 init")
        super().__init__()
    def work(self):
        print("Dummy serial 1 working")
        while(True):
            roundedpowermW = (float("{0:.3f}".format(random.random()
               )))
            self.finished.emit(roundedpowermW)
            time.sleep(1)
### Dummy serial thread 2
class DummySerial2(QObject):
    finished2 = pyqtSignal(float)
    def __init__(self):
        print("Dummy serial thread 2 init")
        super().__init__()
    def work(self):
        print("Dummy serial 2 working")
        while(True):
            roundedpowermW = (float("{0:.3f}".format(random.random()
               )))
            self.finished2.emit(roundedpowermW)
            time.sleep(1)
#### Logging thread
class Logger(QObject):
    logging = pyqtSignal(str)
    loggingStopped = pyqtSignal(str)
    def __init__(self):
```

print("Logging thread init")

```
super().__init__()
        self.is_Logging = True
    def work(self):
        print("Logger working")
        while(self.is_Logging):
            self.logging.emit("1")
            time.sleep(1)
    def stop(self):
        print("Logger stopping")
        self.loggingStopped.emit("1")
        self.is_Logging = False
class MyMplCanvas(FigureCanvas):
    \#\#\# set matplotlib settings here
    def __init__(self, parent=None, width=5, height=4, dpi=100):
        fig = Figure(figsize=(width, height), dpi=dpi)
        fig.patch.set_alpha(0.0)
        self.axes = fig.add_subplot(111)
        #### We want the axes cleared every time plot() is called
        self.axes.hold(True)
        self.compute_initial_figure()
        #### init FigureCanvas
        FigureCanvas.__init__(self, fig)
        self.setParent(parent)
        FigureCanvas.setSizePolicy(self,
                                    QSizePolicy.Fixed,
                                    QSizePolicy.Fixed)
        FigureCanvas.updateGeometry(self)
    def compute_initial_figure(self):
        pass
```

```
class MyDynamicMplCanvas(MyMplCanvas):
    """A canvas that updates itself every second with a new plot."""
    display_length = 200
    #### use a QTimer to update the graph each second
    def __init__(self, *args, **kwargs):
        MyMplCanvas.__init__(self, *args, **kwargs)
        timer = QTimer(self)
        timer.timeout.connect(self.update_figure)
        timer.start(10)
    \#\#\# plot data1 in red, max and min values used for y limits with
        a 10\% offset.
    \#\!/\!/\!\!/\!\!/ also the range can now be set dynamically.
    def update_figure(self):
        self.axes.plot(data1, 'r')
        self.axes.set_xlim(len(data1)-self.display_length,len(data1)
           )
        \#self. ymin = float(min(data1 | len(data1) - self. display length:
           len(data1))) - 0.1*min(data1[len(data1)-self].
           display length: len(data1)))
        #self.ymax = float(max(data1 [len(data1)-self.display length:
           len(data1))) + 0.1*max(data2[len(data1)-self.
           display length: len(data1)))
        #self.axes.set_ylim(self.ymin,self.ymax)
        self.draw()
class MyDynamicMplCanvas2(MyMplCanvas):
    """A canvas that updates itself every second with a new plot."""
    display_length = 200
    \#\#\# use a QTimer to update the graph each second
    def __init__(self, *args, **kwargs):
        MyMplCanvas.__init__(self, *args, **kwargs)
        timer = QTimer(self)
        timer.timeout.connect(self.update_figure2)
        timer.start(10)
```

```
\#\#\# plot data1 in green, max and min values used for y limits
       with a 10\% offset.
    \#\#\# also the range can now be set dynamically.
    def update_figure2(self):
        self.axes.plot(data2, 'g')
        self.axes.set_xlim(len(data2)-self.display_length,len(data2)
           )
        self.ymin = float(min(data2[len(data2)-self.display_length:
           len(data2)]))-0.1*min(data2[len(data2)-self.
           display_length:len(data2)])
        self.ymax = float(max(data2[len(data2)-self.display_length:
           len(data2)]))+0.1*max(data2[len(data2)-self.
           display_length:len(data2)])
        self.axes.set_ylim(self.ymin, self.ymax)
        self.draw()
class Powermeter(QMainWindow):
    def __init__(self, parent=None):
        super(self.__class__, self).__init__()
        self.form_widget = UI(self)
        self.setCentralWidget(self.form_widget)
        #### define a three decimal macro
        self.THREEPLACES = Decimal(10) ** -3
```

create a new thread for power data from power meter 1

 $\#\!\#\!\#\!$ create a new thread for power data from power meter 2

```
self.getPowerThread2 = QThread()
self.getPowerData2 = DummySerial2()
self.getPowerData2.finished2[float].connect(self.
        onDataReceived2)
self.getPowerData2.moveToThread(self.getPowerThread2)
self.getPowerThread2.started.connect(self.getPowerData2.work
        )
self.getPowerThread2.start()
#### Slot to receive the "onDataReceived" signal from the power
        meter 1 power data thread.
```

```
#### Writes recieved data into the first position of data1 and
drops the last element to
```

keep data1 always the same length. Sets the text of currentPowerLabel to the received

value after setting it to three decimals using the THREEPLACES macro defined above.

@pyqtSlot(float)

def onDataReceived(self, powervalue):
 self.form_widget.currentPowerLabel.setText("Current Power 1:
 " + str(Decimal(powervalue).quantize(self.THREEPLACES))
 + " mW")
 data1.append(powervalue)
 if(len(data1) >= 5000):
 del data1[0]

- #### Slot to receive the "onDataReceived2" signal from the power meter 2 power data thread.
- #### Writes recieved data into the first position of data2 and drops the last element to

keep data2 always the same length. Sets the text of currentPowerLabel2 to the received

value after setting it to three decimals using the THREEPLACES macro defined above.

@pyqtSlot(float)

```
def onDataReceived2(self, powervalue2):
    self.form_widget.currentPowerLabel2.setText("Current Power
        2: " + str(Decimal(powervalue2).quantize(self.THREEPLACES
        )) + " mW")
    data2.append(powervalue2)
```

```
if(len(data2) >= 5000):
    del data2[0]
```

```
class UI(QWidget):
```

```
#### open file selector in folder only mode to select log file
folder
```

```
def getDirectoryButtonclicked(self):
    self.logFoldername.setText("Folder where logs will be saved:
        " + QFileDialog.getExistingDirectory(None, 'Select a
        folder:', 'C:\\', QFileDialog.ShowDirsOnly))
    if(self.logFoldername.text() != "Folder where logs will be
        saved: " and self.logFoldername.text() != "Folder where
        logs will be saved: Not set yet"):
        self.logFoldername.setStyleSheet('color: green')
```

def startLoggingButtonclicked(self):

```
\#\!\#\!\#\! add error handling for unset log folder
```

```
if(self.logFoldername.text() == "Folder where logs will be
saved: Not set yet" or self.logFoldername.text() == "
Folder where logs will be saved: "):
MessageBox = QMessageBox.warning(self,"Error:","No
logging folder set yet")
return None
```

 $\#\!\#\!\#$ add error handling for unset log file name

if(self.logFilename.text() == "Select a filename"):
 MessageBox = QMessageBox.warning(self,"Error:","No
 filename set yet")
 return None

```
#### if folder name and file name is set and logging is not
active,
#### start logging thread and set button label to "Stop
logging"
```

if(self.logActive.text() == "Logging: Not active" and self. logFoldername.text() != "Folder where logs will be saved: Not set yet" and self.logFoldername.text() != "Folder
```
where logs will be saved: "):
        self.logActive.setText("Logging: Active")
        self.logActive.setStyleSheet('color: green')
        self.startLoggingButton.setText("Stop logging")
        self.LoggerThread = QThread()
        self.logger = Logger()
        self.logger.logging[str].connect(self.writeLog)
        self.logger.loggingStopped[str].connect(self.stopLog)
        self.logger.moveToThread(self.LoggerThread)
        self.LoggerThread.started.connect(self.logger.work)
        self.LoggerThread.start()
    \#\#\# if logging is active, stop logging thread and set button
        label to "Start logging"
    elif(self.logActive.text() == "Logging: Active"):
        self.logActive.setText("Logging: Not active")
        self.logger.stop()
        self.LoggerThread.quit()
        self.logActive.setStyleSheet('color: red')
        self.startLoggingButton.setText("Start logging")
def __init__(self, parent):
    \#\#\# create tabbed interface
    super(UI, self).__init__(parent)
    tab_widget = QTabWidget()
    tab1 = QWidget()
    tab2 = QWidget()
    tab_widget.addTab(tab1, "Main")
    tab_widget.addTab(tab2, "Advanced")
    #### add label for power meter 1 power data
    self.currentPowerLabel = QLabel(self)
    self.currentPowerLabel.setAlignment(Qt.AlignLeft)
    self.currentPowerLabel.setStyleSheet('font-size: 20pt')
   #### add label for power meter 2 power data
    self.currentPowerLabel2 = QLabel(self)
    self.currentPowerLabel2.setAlignment(Qt.AlignLeft)
```

```
self.currentPowerLabel2.setStyleSheet('font-size: 20pt')
#### add QLineEdit for power meter 1 display length
self.pm1DisplayLength = QLineEdit(self)
self.pm1DisplayLength.setAlignment(Qt.AlignLeft)
self.pm1DisplayLength.setText(str(MyDynamicMplCanvas.
   display_length))
self.pm1DisplayLength.setInputMask("99999")
self.pm1DisplayLength.setFixedWidth(100)
self.pm1DisplayLength.textChanged.connect(self.
   setpm1DisplayLength)
#### add QLineEdit for power meter 2 display length
self.pm2DisplayLength = QLineEdit(self)
self.pm2DisplayLength.setAlignment(Qt.AlignLeft)
self.pm2DisplayLength.setText(str(MyDynamicMplCanvas2.
   display_length))
self.pm2DisplayLength.setInputMask("99999")
self.pm2DisplayLength.setFixedWidth(100)
self.pm2DisplayLength.textChanged.connect(self.
   setpm2DisplayLength)
#### add label for display lenght info 1
self.pm1DisplayLengthLabel = QLabel(self)
self.pm1DisplayLengthLabel.setAlignment(Qt.AlignLeft)
self.pm1DisplayLengthLabel.setText("Number of seconds
   displayed: ")
#### add label for display lenght info 2
self.pm2DisplayLengthLabel = QLabel(self)
self.pm2DisplayLengthLabel.setAlignment(Qt.AlignLeft)
self.pm2DisplayLengthLabel.setText("Number of seconds
   displayed: ")
#### add QLineEdit for log file name
self.logFilename = QLineEdit(self)
self.logFilename.setText("Select a filename")
self.logFilename.textChanged.connect(self.setLogFilename)
```

```
#### add QLabel for log file folder
self.logFoldername = QLabel(self)
self.logFoldername.setText("Folder where logs will be saved:
    Not set yet")
self.logFoldername.setStyleSheet('color: red')
#### add QLabel for log file activity display
self.logActive = QLabel(self)
self.logActive.setText("Logging: Not active")
self.logActive.setStyleSheet('color: red')
#### add QPushButton for folder selector
self.getDirectoryButton = QPushButton(self)
self.getDirectoryButton.setText("Set logging folder")
self.getDirectoryButton.clicked.connect(self.
   getDirectoryButtonclicked)
#### add QPushButton for logging start and stop
self.startLoggingButton = QPushButton(self)
self.startLoggingButton.setText("Start logging")
self.startLoggingButton.clicked.connect(self.
   startLoggingButtonclicked)
#### add MyDynamicMplCanvas for power display of power meter
   1
self.PowerPlot1 = MyDynamicMplCanvas(QWidget(self))
#### add MyDynamicMplCanvas for power display of power meter
   \mathcal{2}
self.PowerPlot2 = MyDynamicMplCanvas2(QWidget(self))
### create Layout
left = QVBoxLayout()
left.addWidget(self.currentPowerLabel, 0)
left.addWidget(self.PowerPlot1, 1)
```

```
displaysettings1 = QHBoxLayout()
displaysettings1.addWidget(self.pm1DisplayLengthLabel, 1)
displaysettings1.addWidget(self.pm1DisplayLength, 1, Qt.
   AlignLeft)
left.addLayout(displaysettings1, 2)
right = QVBoxLayout()
right.addWidget(self.currentPowerLabel2, 0)
right.addWidget(self.PowerPlot2, 1)
displaysettings2= QHBoxLayout()
displaysettings2.addWidget(self.pm2DisplayLengthLabel, 1)
displaysettings2.addWidget(self.pm2DisplayLength, 1, Qt.
   AlignLeft)
right.addLayout(displaysettings2, 2)
top = QHBoxLayout()
top.addLayout(left, 1) \# Both sides take the same amount
   of space.
top.addLayout(right, 1)
main = QVBoxLayout()
main.addLayout(top,0)
main.addWidget(self.logActive, 1)
main.addWidget(self.logFilename, 2)
main.addWidget(self.logFoldername, 3)
main.addWidget(self.getDirectoryButton, 4, Qt.AlignLeft)
main.addWidget(self.startLoggingButton, 5, Qt.AlignLeft)
#### put widgets into the QFormLayout of tab2 here
```

set window title and add tab widget to main window

```
self.setWindowTitle("Power meter")
vbox = QVBoxLayout()
```

```
vbox.addWidget(tab_widget)
    self.setLayout(main)
def setpm1DisplayLength(self, *args, **kwargs):
    if (self.pm1DisplayLength.text() == "" or int(self.
       pm1DisplayLength.text()) == 0):
        setlength = len(data1)
        self.pm1DisplayLength.setText(str(len(data1)))
    else:
        setlength = self.pm1DisplayLength.text()
    MyDynamicMplCanvas.display_length = int(setlength)
def setpm2DisplayLength(self, *args, **kwargs):
    if (self.pm2DisplayLength.text() == "" or int(self.
       pm2DisplayLength.text()) == 0):
        setlength = len(data2)
        self.pm2DisplayLength.setText(str(len(data2)))
    else:
        setlength = self.pm2DisplayLength.text()
    MyDynamicMplCanvas2.display_length = int(setlength)
def setLogFilename(self, *args, **kwargs):
    self.logfilename = self.logFilename.text()
\#\#\# Slot to receive the "go" signal from the logging thread and
   write log file
@pyqtSlot(str)
def writeLog(self, logvalues):
    log = self.logFoldername.text()[33:] + "/" + self.
       logfilename
    logging.basicConfig(filename=log,level=logging.DEBUG,
       filemode="w+", format='%(asctime)s,%(message)s', datefmt=
       '%d.%m.%Y - %H:%M:%S')
    logging.info(self.currentPowerLabel.text()[17:] + "," + self
       .currentPowerLabel2.text()[17:])
\#\!/\!/\!/ Slot to receive the "stop" signal from the logging thread
```

and stop all active loggers

```
@pyqtSlot(str)
def stopLog(self, logvalues):
    log = logging.getLogger()
    for hdlr in log.handlers: # remove all old handlers
        log.removeHandler(hdlr)
def main():
    app = QApplication(sys.argv)
    Interface = Powermeter()
    Interface.show()
    Interface.setFixedSize(Interface.size());
    app.exec_()
if __name__ == "__main__":
    main()
```

Appendix B

List of Publications

- A. Hoffmann, S. Binder, A. Jesser, R. Haase, U. Flörke, M. Gnida, M. Salomone Stagni, W. Meyer-Klaucke, B. Lebsanft, L. E. Grünig, S. Schneider, M. Hashemi, A. Goos, A. Wetzel, M. Rübhausen and S. Herres-Pawlis "Catching an Entatic State - A Pair of Copper Complexes". In: Angewandte Chemie International Edition 53.1, 2014, pp. 299–304
- M. Witte, B. Grimm-Lebsanft, A. Goos, S. Binder, M. Rübhausen, M. Bernard, A. Neuba, S. Gorelsky, U. Gerstmann, G., Henkel, W. Gero Schmidt and S. Herres-Pawlis "Optical response of the Cu₂S₂ diamond core in Cu^{II}₂(NGuaS)₂Cl₂". In: J. Comput. Chem., 2016, 37, pp. 2181–2192.
- A. Hoffmann, J. Stanek, D. Dicke, L. Peters, B. Grimm-Lebsanft, A. Wetzel, A. Jesser, M. Bauer, M. Gnida, W. Meyer-Klaucke, M. Rübhausen and S. Herres-Pawlis "Implications of Guanidine Substitution on Copper Complexes as Entatic-State Models". In: Eur. J. Inorg. Chem., 2016: pp. 4731–4743
- A. Wetzel, F. Biebl, K. Beyerlein, J. Stanek, L. Gumprecht, A. Hoffmann, S. Herres-Pawlis, S. Bajt, H. Chapman, B. Grimm-Lebsanft, D. Rukser and M. Rübhausen "Jet Delivery System for Raman Scattering on Bio-Inorganic Compounds". (submitted to APL)
- 5. B. Dicke, B. Grimm-Lebsanft, et al. "Entatic state for spins, a generalized entatic state concept for spinstate control" (working title, to be published)
- 6. B. Grimm-Lebsanft et al. "Low Temperature Resonance Raman Measurements on in situ Oxygenated Tyrosinase Model Complexes" (working title, to be published)

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