Sigma-Bond-to-Ligand Charge Transfer Transitions and Excited States of d6 Metal-Diimine Complexes.
van Slageren, J.

CHAPTER 2

Research Methods and Backgrounds
2.1 Introduction

In this chapter the most important methods (experimental and theoretical) used for the research described in this thesis are discussed. Firstly, a number of (time-resolved) spectroscopic methods to investigate electronic transitions, the physical properties of the excited state and the product formation and dynamics of photoinduced chemical reactions are discussed. Subsequently, (spectro)electrochemical techniques are briefly introduced. The chapter closes with some information on the quantum chemical calculation methods used in this thesis.

2.2 (Time-Resolved) Spectroscopic Techniques

Traditionally, in order to investigate their mechanisms, photochemical reactions were studied at low temperatures. Apart from studies in conventional solvents, many experiments were performed in liquid xenon or in solid matrices.\(^1\)-\(^3\) Lowering the temperature slows down or stops secondary (thermal) reactions, allowing the primary photochemical steps to be studied by steady-state spectroscopic techniques. The other approach is to use time-resolved techniques. This is the only option for studying excited states and processes that are very fast even at low temperatures. The various (time-resolved) spectroscopic techniques used in this thesis are outlined hereinafter.

2.2.1 Resonance Raman (rR) Spectroscopy.\(^4\)-\(^6\)

If a sample is irradiated with light, most of the photons (if not absorbed or reflected) pass straight through. However, some photons are scattered, due to the dipole which is induced in the molecule by the fluctuating electric field of the light. This is the same phenomenon that is responsible for the blue colour of the sky. The Nobel prize winning observation was that some of the scattered light has a different wavelength from that of the incident light.\(^7\) It was shown that the energy difference is exactly one vibrational quantum. The situation in which the molecule is initially in the zeroth vibrational level of the ground state and ends up in the first excited vibrational level, is called Stokes Raman scattering. In the less common situation that the molecule is initially in the first vibrationally excited state,
we are dealing with anti-Stokes Raman scattering. Scattering can be considered as a two photon process, in which the molecule is taken from an initial to a final state through some intermediate, virtual state (Figure 2.1).

The intensity of the Raman-scattered light is proportional to the square of the polarizability, connected to the mobility of the electrons of the molecule. An interesting situation arises when the energy of the incident light approaches a strongly allowed electronic transition. In this case the polarizability is given by eq. 2.1:

\[
\left< \alpha_{\nu v} \right>_n = \frac{1}{\hbar c} \left| \langle e | M_\sigma | g \rangle \right|^2 \sum_k \frac{\langle f | \nu \rangle \langle \nu | i \rangle}{\nu_{ev} - \nu_{gi} - \nu_{exc} + i \Gamma_{ev}}
\]

where \(g\) and \(e\) are the electronic ground and excited state, respectively; \(i\), \(v\) and \(f\) are the vibrational wavefunctions of initial, virtual and final vibrational levels, and \(\langle e | M_\sigma | g \rangle\) is the electronic transition dipole moment.

Inspection of eq. 2.1 immediately shows that in this situation, the difference between \(\nu_{ev} - \nu_{gi}\) (the frequency difference between a vibrational level of the excited state and the ground state) and \(\nu_{exc}\) (the excitation frequency) becomes very small and hence the polarizability very large. In this case it is assumed that the states involved in the scattering process are only those that the excitation light is in resonance with. A number of other requirements for a large polarizability (and hence a large resonance enhanced Raman intensity) is immediately clear as well: as Raman scattering is a two-photon process, it depends on the square of the electronic transition dipole moment and resonance enhancement is therefore strongest for strongly allowed electronic transitions. Furthermore, since the molecule is normally in a totally symmetric ground state, both the virtual and final vibrational
levels need to be totally symmetric as well, in order for the two overlap integrals in eq. 2.1 to be non-zero. Hence, only bands due to totally symmetric vibrations are observed in rR spectra. These overlap integrals are largest if the ground and excited state potential energy curves are strongly displaced. Therefore, the magnitude of the resonance enhancement of the Raman intensity of a band due to a certain normal vibration increases with increasing distortion along that normal coordinate upon excitation. It is on these last two observations that much of the interpretation of rR spectra in this thesis is based (chapter 3, 4, 6, 7, 8).

Although outside of the scope of this thesis, from careful intensity analysis in combination with computational techniques such parameters as the excited state distortions and vibrational reorganization energies may be extracted.4,8,9

As a light source in our laboratory an Ar+ laser is used in combination with Coherent model CR490 and CR590 dye lasers, employing Stilbene, Coumarin 6 and Rhodamine 6G dyes, giving an excitation range of 430 – 600 nm. Traditionally a very high quality monochromator in combination with a photomultiplier is used. However, in our laboratory the scattered light is detected by a CCD camera, decreasing recording times.

2.2.2 (Time-Resolved) Emission Spectroscopy

Continuous wave (CW) emission spectroscopy typically employs a mercury or xenon lamp as the excitation source. The desired excitation wavelength is selected by a monochromator. The emitted light is passed through a second monochromator, which is scanned through a certain wavelength range. The light is generally detected by a photomultiplier tube. In this way, the emission spectrum is obtained. Keeping the emission monochromator at a set wavelength and scanning the excitation monochromator yields the excitation spectrum. Usually, the luminescence quantum yield is obtained by measuring the integrated emission intensity of the sample and of a reference with known quantum yield under the same conditions, e.g. [Ru(bpy)₃](PF₆)₂ (φₑᵐ = 0.062 in deaerated CH₃CN). Corrections must be made for the absorption at the excitation wavelength, the refractive index of the solvent according to:

\[
\phi_{\text{em}}^s = \phi_{\text{em}}^r \left( \frac{I_s}{I_r} \right) \left( \frac{A_s}{A_r} \right) \left( \frac{n_s}{n_r} \right)^2
\]  

(2.2)

where \( s \) is the sample, \( r \) is the reference, \( I \) is the integrated emission intensity, \( A \) is the absorption at the excitation wavelength and \( n \) is the refractive index of the solvent.
Apart from the luminescence quantum yield and emission maximum, the emission lifetime ($\tau$) is another important parameter. To determine this quantity, time-resolved methods are necessary. These employ pulsed lasers such as nitrogen or Nd:YAG lasers, if necessary in combination with suitable dye lasers. The emission can be measured at a single wavelength using a monochromator and a fast photomultiplier connected to an oscilloscope. Alternatively, a spectrographic detection system (a grating in combination with a diode array or CCD detector) can be used. The detector is 'switched on' for a certain time (the gating time) starting from an arbitrary delay after the laser pulse. This has the advantage that the spectrum is recorded in a single shot rather than point by point. The disadvantage is that for decay analysis the experiment has to be repeated at many different delays in order to make fitting to an exponential function sensible. In this PhD project, such an optical multichannel analysis (OMA) setup was used. The emission spectra were recorded using at least 30 different delay settings, spanning at least three lifetimes. For fitting to biexponential or higher order functions single line measurements should be used. The emission quantum yields, reported in this thesis, were obtained with the same setup as used for the time-resolved measurements. A very long gating time was used to ensure detection of all the emitted photons. Comparison to a reference compound (see eq. 2.2) gave the emission quantum yield. From the emission quantum yield ($\phi_{em}$) and the emission lifetime ($\tau$), the radiative ($k_r$) and non-radiative ($k_{nr}$) decay rate constants can be calculated according to equation (2.3 and 2.4):

$$ k_r = \phi / \tau $$

$$ k_{nr} = 1 / \tau - k_r $$

assuming that the emitting state is populated from the optically occupied one with an efficiency of unity (see section 1.2).

2.2.3 Time-Resolved Absorption Spectroscopy

Apart from determining the parameters for the radiative and non-radiative decay of the excited state, a great deal of information about the excited state can be obtained from its absorption spectrum. The first absorption spectrum of an excited state (of fluorescein in boric acid) was already obtained in 1941. Apart from excited states, transient absorption spectroscopy is also suitable for the study of short-lived photochemical intermediates. The
contemporary setup is similar to the time-resolved emission setup described in the previous section, with the exception that a second light beam is needed to record the actual absorption spectrum (the probe beam). In the nanosecond to microsecond time domain, this is usually a flash lamp. The pump and probe beams can be perpendicular (in this thesis) or nearly collinear. The monitoring light can be detected by a monochromator-photomultiplier combination or alternatively, (this thesis) by the OMA detection system described in the previous section. To correct for variations in the monitoring light intensity a reference monitoring beam is needed in the latter type of setup. Both monitoring beams are transferred via optical fibers to the CCD detector and their intensities are recorded at the same time. It is possible to direct both beams through the same cuvette, while exciting only one part, using e.g. 1.0 mm holes for the monitoring beams and a 1 cm slit for the pump beam. It was found in our laboratory that employing a 50% mirror to divide the monitoring light, sending one part through the excited sample and one part through a reference cuvette greatly improved the signal-to-noise ratio. This is due to variable inhomogeneity of the monitoring light spot. Using the 50% mirror, the same part of this spot is used for both sample and reference beams, thus eliminating that part of measurement noise. Figure 2.2 shows a schematic representation of the setup used.

![Diagram](image)

Figure 2.2 Schematic setup for transient absorption measurements.

Since most of the complexes studied are photolabile to a certain extent, a flow-through system had to be employed. To this end the outer compartments of two (sample and reference) thermostatable cuvettes (Hellma 160.001-QS) were connected in series to a pump (Verder 2040). At least 30 mL of solution was circulated through this closed system.
2.2.4 Time-Resolved Infrared (TRIR) Spectroscopy\textsuperscript{12-15}

Most of the complexes described in this thesis bear carbonyl ligands. The frequencies of the stretching vibrations of carbonyl ligands ($v$(CO)) are very sensitive to the electronic and molecular structure of the complex. Moreover, the extinction coefficients of absorptions due to these vibrations are high and the carbonyl stretching region of the infrared (IR) spectrum is relatively transparent. This makes IR-spectroscopy an excellent tool for investigating carbonyl complexes. Since excited states and primary photoproducts are often short lived, time resolved IR spectroscopy is a convenient means for their study.

Over the past decade TRIR spectroscopic techniques have evolved enormously. Many TRIR studies of transition metal complexes have been concerned with their MLCT excited states. It was shown that the carbonyl stretching vibrations normally shift to considerably higher frequencies going to an MLCT state, since lowering the electron density on the transition metal atom decreases the metal–CO π-backbonding. Much smaller shifts of the $v$(CO) frequencies have been observed for the IL excited state of $[\text{Re}(\text{PPh}_3)(\text{CO})_3(\text{dppz})]$\textsuperscript{16}, the L’LCT (L’ = I) excited state of $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(\text{iPr–DAB})]$\textsuperscript{17} and the SBLCT excited states of $[\text{Re}(\text{Bz})(\text{CO})_3(\text{iPr–DAB})]$\textsuperscript{18} and $[\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(\text{iPr–DAB})]$. In these cases the metal is not or hardly involved in the electronic transition. The $v$(CO) bands may then even shift to lower frequencies since the α-diimine ligand is a weaker π-acceptor in the excited state, compared to the ground state, increasing the metal–CO π-backbonding in the excited state.

Initially, TRIR spectra were recorded using tunable IR lasers and fast IR detectors. In the last few years, step-scan Fourier Transform IR has been increasingly used to this end.\textsuperscript{20} Recently, sub-picosecond time resolutions have been achieved by pump-probe methods similar to those used in ultrafast transient electronic absorption spectroscopy.\textsuperscript{12}

2.2.5 Electron Paramagnetic Resonance (EPR)\textsuperscript{21}

The essential requirement for a compound to be EPR active is the presence of one or more unpaired electrons. Apart from stable radicals, reactive radical species can be generated e.g. by (electro)chemical one-electron reduction or oxidation of a diamagnetic parent species, or by photoinduced chemical processes such as bond homolysis or electron transfer. Unstable radical species can be transformed into relatively stable radicals by reaction with e.g. nitroso compounds, that give stable radical adducts. This is called the spin-trapping technique.
EPR spectroscopy is based on the fact that the energies of the two electron spin levels are inequivalent in a magnetic field, separated by the so-called Zeeman splitting. When the molecule is irradiated with microwaves of an energy corresponding to the energy difference between the spin levels, absorption of radiation can occur. The resonance condition is:

\[ h \nu = g \mu_B B \]  

where \( B \) is the magnetic field, \( \mu_B \) is the Bohr magneton \((9.273 \times 10^{-24} \text{ JT}^{-1})\), and \( g \) is the \( g \) value, which is comparable to the chemical shift in NMR. This \( g \) value is 2.0026 for a free electron. The observed \( g \) value for a radical deviates from this value, if the applied magnetic field induces a local electric current. Nuclei with non-zero spin quantum numbers induce a local magnetic field at the position of the unpaired electron, due to their nuclear spin. Consequently, the resonance line is split into a number of lines corresponding to the number of possible spin orientations of the nucleus. This phenomenon is called hyperfine splitting. It is on this effect that much of the merit of the EPR technique is based, since the magnitude of this splitting effect, the hyperfine splitting constant, depends on the distance between the nucleus and the unpaired electron. Hence determination of the hyperfine splitting constants gives information about the electronic structure of the studied paramagnetic species.

Typically, commercial instruments use a klystron as microwave source, that operates at a set frequency, usually at ca. 10 GHz (the X-band of microwave radiation). The corresponding magnetic field (of ca. 0.3 T) is produced by an electromagnet. The EPR spectrum is recorded by sweeping the magnetic field and observing the change in absorption of microwave radiation. To improve the signal-to-noise, the field is usually modulated (typically at a 100 kHz frequency) with an amplitude less than the resolution desired, due to which the EPR spectrum is obtained as its first derivative.

2.2.6 Fourier-Transform Electron Paramagnetic Resonance (FT-EPR)\(^{22-24}\) and Chemically Induced Dynamic Electron Polarization\(^{25,26}\)

The short lifetime of free radicals created a need for time-resolved methods in EPR spectroscopy as well. Whereas the lower intrinsic sensitivity of NMR compared to EPR, resulted in the development of Fourier Transform (FT) NMR techniques at an early date, this development has been relatively slow in EPR. As the principles are identical, they can be found in any FT-NMR textbook. Briefly, a short pulse of electromagnetic radiation causes 90° change of the magnetization direction from the z-axis (the direction of the external magnetic
field) to the xy-plane. The magnetization, which now rotates in the xy-plane, induces an alternating current in the receiver coil. With time the magnetization returns to the equilibrium direction and the signal fades. This free induction decay (FID) represents the spectrum of the paramagnetic species in the time domain. Fourier transformation yields the spectrum in the frequency domain (Figure 2.3).\textsuperscript{23}

![Figure 2.3 Example of free induction decay (FID) recorded after a 90° microwave pulse and the frequency domain spectrum of a radical obtained after Fourier transformation.](image)

The actual FT-EPR spectrometer used has been described.\textsuperscript{24,27} The generated microwave radiation is amplified by a travelling wave tube amplifier (TWT), that generates 1 kW microwave pulses (of \textit{ca.} 15 ns duration) which pass through a variable attenuator into the microwave cavity. The microwave signal generated by the sample is frequency down converted by mixing with a reference signal from the microwave source in a quadrature IF mixer. The two-channel output (corresponding to the FID of the magnetization along the x- and y-axes) is fed to a digital oscilloscope. A CYCLOPS phase cycling routine is used to correct for imperfect quadrature detection. Typically 100 FIDs per phase (400 in total) are averaged by the oscilloscope before transfer to the controlling computer. The phase of the output signal is slightly dispersive, which can be corrected for by using a stable radical
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reference. The spectral bandwidth covered by a single microwave pulse is limited by inequality 2.6:

\[ |\omega_{\text{res}} - \omega_{\text{mw}}| < \gamma e B_1 \]  

(2.6)

in which \( \omega_{\text{res}} \) and \( \omega_{\text{mw}} \) are the resonance and applied microwave frequencies, respectively, and \( \gamma e \) is the gyromagnetic ratio of the electron spin and \( B_1 \) is the strength of the microwave field.

For the equipment used, this yields a bandwidth of 12 G. Hence, spectra covering more than this range must either be corrected for loss in intensity or obtained at several field settings. Another limitation of the equipment is that during the first 120 ns after the microwave pulse, no signal can be recorded due to cavity ring-down. In practice this limits the applicability of the technique to radicals with a line width of less than 1 G. By linear prediction singular value decomposition (LPSVD), which is based on the assumption that the FID can be represented as the sum of a number of exponentially damped sinusoids, the missing part of the FID can be reconstructed. This results in an increase of signal-to-noise, but can create artifacts in the frequency-domain spectrum.

In the studies described in this thesis the radicals were generated by a pulsed laser. By varying the delay between laser and microwave pulses, information about the radical kinetics can be obtained. Importantly, the FID represents the time-domain spectrum of the radicals present at the time of the microwave pulse. Any radical formation or decay during FID recording only causes line broadening in the frequency domain spectrum. An effect of the short time delay between radical formation and measurements is that the spin distribution may deviate from Boltzmann equilibrium values. The spin distribution will eventually decay to the Boltzmann equilibrium through spin–lattice relaxation (after several microseconds). Processes that create non-Boltzmann electron spin distributions are collectively known as chemically induced dynamic electron polarization (CIDEP) mechanisms. The mechanisms that are important in this thesis are outlined below. More mechanisms exist, notably those in which a (stable) radical interacts with a triplet excited state,\(^{25}\) but these are not discussed here.

Hyperfine dependent CIDEP mechanisms

\( ST_0 \) Radical Pair Mechanism (\( ST_0 \) RPM)

A photochemically generated geminate radical pair is created with singlet or triplet character depending on the spin multiplicity of the excited state which it originates from. The
energies of the two spin states of the radical pair are separated by twice the exchange interaction ($J$). Since the singlet radical pair state is considered the bonding state, $J$ is negative for neutral radical pairs. In the case of radical ion pairs indications for positive signs of $J$ have been obtained. The exchange interaction is far too large for any efficient interaction to occur between the singlet and any of the triplet sublevels. However, if the radicals diffuse apart within the solvent cage, the exchange interaction, which depends on the overlap of the unpaired electron orbitals, rapidly decreases until the singlet (S) level and the T$_0$ component of the triplet level are degenerate (Figure 2.4). At this point the hyperfine interaction may induce differences in precession frequencies of the two radicals and mixing between the S and T$_0$ spin levels occurs. However, the magnetic hyperfine interaction itself cannot create spin polarization, whereas exchange interaction can. Hence a re-encounter of the two radicals in the solvent cage is needed. This process can be repeated, increasing the generated polarization. Thus the magnitude of the generated polarization depends on the time the radical pair spends in the solvent cage and hence it is expected to increase with increasing solvent viscosity. The sign of the polarization in one hyperfine component of the EPR spectrum depends on the sign of the exchange interaction and the spin multiplicity of the excited state precursor. This leads to the general observation that for a negative exchange energy and a triplet precursor, low field peaks are in emission and high field peaks are in absorption. The magnitude of the spin polarization of a certain hyperfine component depends on the difference in resonance frequencies between that hyperfine component and the hyperfine components of the other radical of the pair. Finally it must be noted that ST$_0$ mixing does not create net spin polarization, but rather redistributes spins of the two radicals of the pair.

**ST$_{-1}$ Radical Pair Mechanism (ST$_{-1}$ RPM).**

It can be seen from Figure 2.4 that mixing between the S and T$_{-1}$ levels is also possible. However, since the mixing region is small, it has been generally assumed that this type of RPM is only important for systems with large hyperfine interactions or in viscous solvents (in which the radicals are kept in close proximity for a long time). Due to the need for total angular momentum conservation, a hyperfine-interaction-induced nuclear spin flip has to occur simultaneously with the electron spin flip (in the opposite direction and on the same radical). If the radical pair is initially formed in the T$_{-1}$ (ββ) state no nuclear spin flip can occur for the all-β nuclear spin state. For a positive hyperfine interaction, this means that the highest field line has a zero contribution from this mechanism. There is another, hyperfine-
independent part, that contributes to ST₋₁ polarization. This is due to the fact that one of the radicals in its particular hyperfine state may interact with the other radical in all of its hyperfine states, giving rise to a net emission polarization for a triplet state precursor. Combined, the polarization pattern due to the ST₋₁ RPM for a triplet state precursor is totally emissive with a stronger polarization for the lowest field line than for the highest field one.

**Figure 2.4** Diabatic potential energy curves of the singlet (S) and triplet levels of a radical pair, separated by twice the exchange energy (J) as a function of interradical distance. ST₀ and ST₋₁ indicate positions at which hyperfine interaction induced mixing may occur between mentioned levels.

**Hyperfine independent CIDEP mechanisms**

*Triplet Mechanism (TM)*  
As was mentioned in chapter 1, intersystem crossing (ISC) rates depend on the symmetries of the states involved, as well as on that of the spin–orbit coupling Hamiltonian. In the absence of a magnetic field the three triplet states (Tₓ, Tᵧ and T₂) are not degenerate due to dipolar coupling of the two electrons. This means that in the absence of a magnetic field ISC can be anisotropic, *i.e.* one of the triplet sublevels is populated preferably (Figure 2.5). In a magnetic field the triplet sublevels are governed by the direction of this field. Since the molecule rotates in solution, no preferential population of any of the triplet sublevels (T₀, T±₁), separated by the Zeeman splitting, is expected. However, since for organic molecules in the magnetic field of an X-band spectrometer, the zero-field and Zeeman splittings are of the same order of magnitude, some correlation between the two descriptions of the triplet states does exist. This correlation becomes stronger when the rotational correlation time is increased, *i.e.* in more
viscous solvents. The excess population of one of the triplet sublevels translates into excess population in one of the spin levels of the free radical (Figure 2.5), creating a net emission or absorption effect in the EPR spectrum. However if the radical formation is slower than the spin–lattice relaxation decay (typically a few nanoseconds) of the triplet spin polarization, no TM spin polarization is observed. Then, the spin distribution in the free radicals depends on the Boltzmann equilibrium spin distribution in the triplet excited state. On the other hand, if the triplet excited state is too short-lived, i.e. shorter than the order of one precession turn (100 ps at 10 GHz), the energies of the triplet sublevels become uncertain and again no spin polarization in the free radicals is generated. This creates a time window that the photochemical reaction rate has to be in, in order for the TM to operate.

**Figure 2.5** Schematic overview of the important processes in the Triplet Mechanism (TM) induced spin polarization.

**Spin–Orbit Coupling Mechanism (SOCM)**

The radical pair in its triplet state can only convert to its singlet state by intersystem crossing when in close contact. Since ISC-rates are spin-sublevel selective, this leads to selective depopulation of some of the triplet sublevels in the contact radical pair. If the remaining triplet contact radical pairs subsequently proceed to disintegrate into free radicals, hyperfine independent spin polarization will have been generated. This mechanism can be distinguished from the TM, since in SOCM the presence of heavy atoms will increase the polarization, but decrease the radical formation yield.
2.3 (Spectro)electrochemistry

Since in photochemical and redox reactions the same (frontier) orbitals may be involved, data from reversible electrochemical processes can supplement those from photochemical measurements. For instance, the difference between reduction and oxidation potentials is often used as an indication for the energy difference between the zeroth vibrational levels of ground and excited states. Furthermore, some photoproducts (e.g. radicals) can be conveniently generated by electrochemical methods and transient species (e.g. D$^+$−A$^-$ states) observed in time-resolved spectra can be assigned by recording the spectra of electrochemical oxidation and reduction of the donor and acceptor moieties, respectively. Finally, in situ electrogenerated species may have interesting photophysical and photochemical properties themselves.

The commonly used method for the determination of oxidation and reduction potentials is cyclic voltammetry (CV). In this experiment the voltage applied to a sample solution with added electrolyte is scanned, while recording the current. At a certain predefined potential the scan direction is reversed (hence: cyclic voltammetry). Initially, assuming no electrode process occurs and the solution resistance is close to zero, no current flows. Once the potential reaches a value at which the sample compound is oxidized or reduced, the current rises. Since the solution is not stirred, the concentration of the parent compound in the thin layer near the working electrode surface (the electrode double layer) decreases. At a certain potential the concentration gradient is steepest and the diffusion-controlled Nernstian current reaches a maximum. The parent compound has then been exhaustively electrolyzed at the electrode surface. Continued sweeping of the potential shifts the zone of electrolysis further to the bulk solution, the concentration gradient drops again and the Faradaic current decreases exponentially to the mass transport limiting value. Figure 2.6 displays a typical example of a cyclic voltammogram. Apart from a working electrode and a counter electrode, some means must be devised to determine the applied potential. For the CV measurements presented in this thesis, a silver wire was employed as a pseudo-reference electrode. Since the potential of such an electrode varies with temperature and chemical composition of the solution, all potentials are given relative to the redox potential of the Fc/Fc$^+$ couple (Fc = ferrocene) used as an internal standard. Many types of absolute reference electrodes exist, e.g. saturated calomel electrodes (SCE). However, these suffer
from the disadvantage that they cannot be used in air-tight, evacuable CV-cells of the type used in this thesis.

![Cyclic voltammogram](image)

**Figure 2.6** Typical example of a cyclic voltammogram.

CV does not provide any specific information on bonding and electronic properties. However, since oxidized and reduced species have their own spectroscopic (UV/Vis, IR, EPR, resonance Raman, etc.) properties, the combination of cyclic voltammetry and spectroscopic techniques is a powerful one. Spectroelectrochemistry (IR, UV/Vis) has advanced hugely since the development of optically transparent thin layer electrochemical (OTTLE) cells. The working electrode of such a cell usually consists of a transparent wire mesh, rather than a solid surface.\(^{42,43}\) Spectroelectrochemical techniques at various temperatures are used in chapter 4.

### 2.4 Quantum chemical calculations\(^ {44,45}\)

#### 2.4.1 Introduction

The investigations described in this thesis make use of quantum chemical calculations in several instances, in order to clarify the electronic structure of the complexes under study, to assign low-lying electronic transitions and to assign bands observed in resonance Raman spectra. This section attempts to give a very brief introduction in quantum chemical calculations in general and density functional methods in particular.
In quantum chemical calculations one generally aims to solve the famous Schrödinger equation (eq. 2.7):

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

in which

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i\neq j} \frac{1}{|r_i - r_j|} \]

Although elegant in its simplicity, it is analytically unsolvable for multi-electron systems. The first two terms of the Hamiltonian, describing the kinetic energy of the entire system and the potential energy due to the electrostatic interaction of the electrons with the nuclei do not pose any problems, in contrast to the third term, which describes the electron–electron interaction. Hence, the aim is to approximate this electron–electron interaction in such a way that the equation can be solved, while at the same time giving reliable results. In \textit{ab initio} methods, once an approximate model for the molecular electronic wavefunction has been obtained, one proceeds to perform the calculations rigorously without further approximations. As this gives rise to lengthy calculations especially for large molecules, simplified methods have been developed in which experimental information is used in the calculation to obtain accurate information about electronic structures and so on. These latter methods are collectively known as semi-empirical methods.

A common first approximation of the electron–electron interaction is that each electron moves in an average field of the other electrons. In this way the n-electron equation can be separated into n one-electron equations. A frequently used way to solve these equations is by the self-consistent field (SCF) method, starting with a set of guess orbitals from which the operator can be constructed. Solution of the n one-electron equations yields a new set of orbitals, which can in turn be used to adjust the operator. This iterative process continues until the obtained orbitals remain constant.

However, by approximating the electron–electron interaction as described above, it was assumed that each electron moves independently, thus neglecting electron correlation. Several ways have been developed to make post-SCF corrections that approximate electron correlation in some way, such as configuration interaction (CI) and Møller-Plesset
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perturbation methods, e.g. MP2. The calculations described in this thesis were performed by a different approach, known as density functional theory.

2.4.2 Density Functional Theory \(^{46,47}\)

Density functional theory (DFT) deals with electron densities rather than wavefunctions. This theory is based on the theorem that the total energy of a system is a functional of the system’s electron density.\(^{48}\) In general a functional is the integration of a function over space. If this function contains first or higher derivatives, integration yields a non-local functional.

Rather than solving the Schrödinger equation, in DFT-calculation the aim is to minimize the energy functional, which reduces calculational costs enormously, compared to conventional \textit{ab initio} methods. This energy functional can be written as a sum of functionals describing the kinetic energy, the electrostatic interaction between electrons and nuclei, the repulsion of each electron moving in the average field of all the other electrons and, finally, the electron exchange and correlation interaction.\(^{49}\) A self-consistent field approach (see above) can be taken to perform the calculation. The last term, the electron exchange and correlation energy functional has to be approximated and it is the quality of this approximation that determines the quality of the results of the calculation. A popular method is the local density approximation, in which one assumes that the system can be approximated locally by a homogeneous electron gas. Additionally, more accurate functionals have been developed, on which most of the success of the DFT-method is based. Another important factor is the choice of basis sets; molecular orbitals can be represented by a linear combination of one-electron orbitals or basis functions, which is called the basis set. A great deal of effort is being put into the development of better basis sets. Over the last 20 years, time-dependent DFT-methods were developed,\(^{50}\) which have been implemented recently in some program packages. These methods, which give access to properties such as Raman intensities and excitation energies are also used in chapter 7 of this thesis.
2.5 References

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