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From solution to solid state: energy- and electron-transfer in complex materials

d'Aléo, A.

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Chapter 8

Instrumentation and experimental methods

Abstract

In this Thesis, several different techniques were used in order to characterize ground state (inspected by light or electric current) and excited states behaviour, non-linear properties or only for imaging nanoparticles. In this Chapter, the methods used are briefly described. The set-up used as well as the location is specified. Conditions for other techniques (NMR, pump freezing for deaerating, cleaning and preparation of coated surfaces) are given in the separate chapters.
8.1 Steady State Absorption and Emission Measurements

Electronic absorption spectra were recorded in a quartz cuvette (1 cm, Hellma) on Hewlett-Packard 8543 diode array spectrometer (range 190 nm-1100 nm). Steady state fluorescence spectra were recorded using a spex 1681 fluorimeter, equipped with a Xe arc light source, a Hamamatsu R928 photomultiplier tube detector and double excitation and emission monochromator. Emission spectra were corrected for source intensity and detector response by standard correction curves, unless otherwise noted. Emission quantum yield are measured in optically dilute solutions, using the indicated reference solution in the individual chapters, according to the following:

\[ \Phi_u = \frac{(A_r I_u n_u^2)}{(A_u I_r n_r^2)} \Phi_r \]  

(Eq 8.1)

where \( u \) and \( r \) are the unknown and the reference respectively, \( \Phi \) is the luminescence quantum yield, \( A \) is the optical absorbance at the excitation wavelength (\( \approx 0.1 \)), \( I \) is the integrated emission intensity and \( n \) is the refractive index of the solvents.

The fluorescence microscopy images were measured in Munster using an epi-fluorescence microscope (Axioplan, Germany), equipped with a 63x long distance objective (NA 0.90) and standard fluorescence filter sets, was used. Images were taken by a CCD camera (KAPPA, Germany), digitized by a frame-grabber card, and processed by imaging software.

8.2 Time Resolved Spectroscopy Measurements

8.2.1 Time Resolved Fluorescence

a- Nanosecond time scale

Lifetimes of excited states were determined using a coherent Infinity Nd:YAG-XPO laser (2 ns pulses fwhm) and a Hamamatsu C5680-21 streak camera equipped with Hamamatsu M5677 low speed single sweep unit. Streak cameras are high-speed light detectors, which enable detection of the fluorescence as a function of the spectral and the time evolution simultaneously.
Time resolved fluorescence measurements were performed using a picosecond time-correlated single photon counting (SPC). The complete set-up (Figure 1) has been described elsewhere.\cite{1} A mode-locked Argon-ion laser (Coherent 486 AS Mode Locker and Coherent Innova 200 laser) was used to pump DCM dye laser (Coherent model 700). The output frequency was doubled with a BBO crystal and the 323 nm pulse was used as excitation. A microchannel plate photomultiplier (Hamamatsu R3809) was used as the detector. The instrument response (fwhm= 17 ps) was recorded using the Raman band of a doubly deionized water sample. Time windows (4000 channels) of 5ns (1.25 ps/channel) – 50 ns (12.5 ps/channel) could be used allowing a window for measurements going from 5 ps to 40 ns. The recorded decay traces were deconvoluted with the system response and fitted using the computer program FluoroFit (PicoQuant).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic representation of picosecond single photon counting (SPC) setup: 1. mode locker, 2. Ar\textsuperscript{-}ion laser, 3. dye laser, 4. cavity dumper, 5. autocorrelator, 6. photodiode, 7. sample, 8. monochromator, 9. photomultiplier, 10. photocounting system and 11. computer}
\end{figure}

\subsection*{8.2.2 Time Resolved Absorption}

Transient absorption (TA) measurements represent a form of differential spectroscopy. It relies on recording electronic absorption spectra of transient species (excited molecules or photoproducts) at selected time delays after the excitation pulse. The transient absorption
signal can either be recorded over an extended wavelength range (full spectrum) or at a single wavelength.

a- Nanosecond time scale

Nanosecond transient absorption spectra were obtained by irradiating the samples with 2 ns pulses (fwhm) of a continuously tunable (420-710 nm) Coherent Infinity XPO laser. The output power of the laser was typically less than 5 mJ/pulse at a repetition rate of 10 Hz. Samples in a 1 cm quartz cuvette with ca. 0.8 optical density at the excitation wavelength. The probe light from a low-pressure, high-power EG&G FX-504 Xe lamp passed through the sample cell and was dispersed by an Acton Spectra-Pro-150 spectrograph, equipped with 150 g/mm or 600 g/mm grating and a tunable slit (1-500 μm) resulting in 6 or 1.2 nm maximum resolution, respectively. The data collection system consisted of a gated intensified CDD detector (Princeton Instruments ICCD-576EMG/RB), a programmable pulse generator (PG-200), and an EG&G Princeton Applied Research Model 9650 digital delay generator. With OMA-4 setup (see Figure 2), I and I₀ values are measured simultaneously, using a double kernel 200 μm optical fiber.

![Figure 2. Schematic representation of the nanosecond transient absorption setup: 1. laser, 2. Xe lamp, 3. sample, 4. spectrograph, 5. CCD camera, 6. pulser and 7. computer](image)

b- Sub-picosecond time scale

The setup used for the sub-picosecond transient absorption measurements is shown in Figure 3. The laser system is based on a Spectra Physics Hurricane Ti-sapphire regenerative amplifier system. This optical bench assembly of the Hurricane includes a seeding pump laser (Mai Tai), a pulse stretcher, a Ti-sapphire regenerative amplifier, a Q-switched pump laser (Evolution) and a pulse compressor. The output power of the laser is typically 1 mJ/pulse.
(130 fs fwhm) at a repetition rate of 1 kHz. The pump probe setup employed a full spectrum setup based on two optical parametric amplifiers (Spectra-Physics OPA 800) as a pump (depending on the excitation wavelength) and a residual fundamental light (150 μJ/pulse) from the pump OPA was used for the generation of white light, which was detected with CCD spectrograph. The OPA was used to generate excitation pulses from 280 – 600 nm (fourth harmonic signal of the OPA or idler). The white light generation was accomplished by focusing the fundamental (800 nm) into a stirred water cell equipped with barium bisfluoride or sapphire windows. The pump light was passed over a delay line (Physik Instrumente, M-531DD) that provided an experimental time window of 1.8 ns with the maxima resolution of 0.6 fs/step. The energy of the probe pulses was ca. 5 x 10^{-3} mJ/pulse. The angle between the pump and the probe beam was typically 7 - 10°. Samples were prepared in quatz cuvette (l = 0.1 cm) to have an optical density of ca. 0.8 at the excitation wavelength. For the white light/CCD setup, the probe beam was coupled into a 400 μm optical fiber after passing through the sample, and detected by a CDD spectrometer (Ocean Optics, PC2000). The chopper (Roffin Ltd., f = 10 – 20 Hz), place in the excited state spectra were obtained by $\Delta A = \log (1 / I_0)$. Typically, 2000 excitation pulses were averaged to obtain the transient at a particular time. Due to the lenses, a chirp of ca. 1 ps is observed between 460 – 650 nm.

![Figure 3. Schematic representation of the sub-picosecond transient absorption setup: 1. Hurricane, 2. OPA-800, 3. delay line, 4. white line generator, 5. Berek polarizer, 6. chopper, 7. sample and 8. CCD camera](image-url)
8.2.3 Confocal Microscopy

Laser scanning confocal microscopy represents one of the most significant advances in optical microscopy ever developed, primarily because the technique enables visualization deep within both living and fixed cells and tissues and affords the ability to collect sharply defined optical sections from which three-dimensional renderings can be created. Development of modern confocal microscopes has been accelerated by new advances in computer and storage technology, laser systems, detectors, interference filters, and fluorophores for highly specific targets.

Figure 4. Principle of a confocal microscop

The principle of such microscop can be schemed as in Figure 4. The light is emitted by a laser through a pinhole. The light is then reflected by a dichromatic mirror on the sample in the focal plan. The response is detected by a photomultiplier detector.

Confocal microscopy images were obtained with a MicroTime 200 fluorescence lifetime microscope system (Picoquant) coupled to an Olympus IX71 inverted microscope. The excitation source consisted of a pulsed blue-diode laser (PDL 800-B, PicoQuant Berlin) with a wavelength of 440 nm, providing output pulses of < 100 ps. All measurements were conducted in a dark compartment at room temperature in air.

8.3 Non Linear Optic (NLO) Measurements (ENS Cachan)

The experiments were performed in Cachan. The principle of the HLS is described in Chapter 5 together with the background on NLO.
Harmonic Light Scattering (HLS)

The 1.91 μm fundamental beam was emitted by a high-pressure (30 bar), 50 cm long Raman cell pumped by Nd3+: YAG laser operating at 1.06 μm (or 1.34 μm) with a 10 Hz repetition rate and pulse of 15 ns duration. Only the back-scattered 1.91 μm Raman emission was collected at a 45° incidence angle by use of dichroic mirror in order to eliminate most of the residual 1.06 μm pump photons (Figure 5).

The HLS photon at 955 nm were focused onto a photomultiplier tube (Hamamatsu R632-01 photomultiplier tube) by two collecting lenses. The detected signal was then sampled and averaged by a boxcar, and processed by a computer. The reference beam was collected at 45° incidence angle by a glass plate, and focused onto a highly nonlinear NPP powder, which was used as the frequency doubler. The variation of the scattered second harmonic intensity from the solution was recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder, which scales as the square of the incoming intensity. Value for β were then inferred from the slopes of the resulting lines.

![Figure 5. Experimental setup of HLS measurements](image)

8.4 Electrochemistry

Cyclic, differential pulse and square wave voltammetric scans were performed with a gastight single-compartment cell under an atmosphere of dry nitrogen or argon. The cell was equipped with a Pt disk working (apparent surface area of 0.42 mm²), Pt wire auxiliary and
Ag wire pseudoreference electrodes. The working electrode was carefully polished with 0.25 μm-grain diamond paste between scans. The potential control was achieved with a PAR Model 283 potentiostat. All redox potential are reported against the ferrocene-ferrocnium (Fc/Fc⁺) redox couple used as internal standard\(^4\) \((E_{1/2} = 0.38 \text{ V vs. SCE in acetonitrile})\). Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) was used as support electrolyte. All electrochemical samples were 5 \times 10^{-4} \text{ M in the studied complex and contained 3 \times 10^{-1} M of Bu₄NPF₆.}

For chapter 6, the electrochemistry was performed in Warwick where cyclic voltammetry (CV) measurements were made in a three-electrode arrangement using an electrochemical analyser (CH Instruments, model CHI 400). A platinum wire was always used as the counter electrode. Different working electrodes were employed, such as ITO (0.14 cm²), a platinum disk (1.6 mm diameter, area 0.02 cm²) and both platinum and gold thin films deposited on glass (100 nm thick, area 0.25 cm²). A saturated calomel electrode (SCE) was used as the reference electrode in aqueous solutions and an Ag/AgNO₃ reference electrode (157 mV vs. SCE) was employed in 0.1 M Bu₄N ClO₄/acetonitrile solutions.

8.5 High Resolution Transmission Electron Microscopy (HR-TEM)(TU Delft)

TEM (Transmission Electron Microscopy) is a method of producing images of a sample by illuminating the sample with an electron with energy between roughly 100 and 300 keV (in vacuum), and detecting the electrons that are transmitted through the sample.

In Figure 7, the comparison of light and electron microscopes is made. In both instruments, illumination from the source (lamp, filament in the electron gun) is focused by the condenser lens onto the specimen. A first magnified image is formed by the objective lens. This image is further magnified by the projector lens onto a fluorescent screen, CCD camera or photographic plates (electrons) instead of a ground glass screen (light).

HR-TEM, Cross sectional TEM electron micrographs have been taken with a Philips CM30T, and a CM300UT-FEG, both operating at 300 kV. A drop of a dilute suspension of particles was placed on a copper grid with a carbon foil and the solvent was, subsequently, evaporated at room temperature and atmospheric pressure.
Instrumentation and experimental methods

Figure 7. Comparison of light and electron microscopes.

8.6 References
