Neutron photocryystallography: simulation and experiment

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Abstract. The investigation of light-induced structural changes by diffractive methods has improved significantly in the last two decades. We present here the case of neutron photocryystallography for which we have built a special experimental setup at the single crystal neutron diffractometer TriCS at the Swiss Spallation Neutron Source SINQ. We illustrate the progress of the method on the example of the structural determination of photoinduced nitrosyl linkage isomers in Na2[Fe(CN)5NO]·2H2O. The in-situ determination of the population of the light-induced linkage isomers by optical transmission measurements enhances the reliability of such structural investigations considerably. Additionally we present a new simulation tool within the program package JANA2006 which allows to plan a photocryystallographic experiment thoroughly since the required q-range, the minimally needed population of the photoinduced species, as well as the necessary counting statistics for a successful single crystal diffraction experiment can be evaluated in advance.

1. Introduction

Reversible photoinduced chemical reactions or structural changes have received much attention in the last decades due to the possibility to trigger such changes by laser pulses which allows for a targeted investigation of the fundamental underlying processes, e.g. charge transfer processes or isomerisation reactions ([1–5] and references therein). In this manner structures and chemical complexes become accessible which cannot be realized by standard synthetic methods. Static neutron diffraction experiments investigating light-induced structural changes were started on the optically switchable system Na2[Fe(CN)5NO]·2H2O (SNP) [6] which is of interest due to its outstanding photo-refractive properties [7]. In SNP two metastable linkage isomers, labelled SI and SII, of the NO-ligand are generated by light irradiation in the blue-green spectral range as illustrated in Fig. 1 [3, 8]. The first structural investigation of the metastable states in SNP was performed by neutron diffraction [6], which found a small increase in the Fe–N bond length. This result was later confirmed by X-ray diffraction [9], but did not satisfactorily explain the long lifetime of the metastable states [10]. In 1997 a breakthrough in the understanding of this kind of metastable states was made by the X-ray diffraction study of Carducci et al. [11] and the calculations based on density functional theory (DFT) by Delley et al. [12], which showed that in SI the NO ligand is rotated by 180° (isonitrosyl) and in SII it is rotated by 90° (side-on configuration). Surprisingly a following neutron diffraction study failed to confirm the isonitrosyl configuration for SI in SNP [13]. Only recently two neutron diffraction studies on the states SII [14] and SI [15] unambiguously confirmed the linkage-isomer character of the metastable states in SNP. For this success a series of experimental improvements were necessary, which will be discussed in this paper.

Today, X-ray diffraction is used for most of the photocryystallographic experiments, but improved neutron diffraction investigations have been proven to be especially suited for the investigation of light-induced linkage isomers due to the following reasons: (i) the neutron is a low energy probe, i.e. it does not destroy the light induced...
species, (ii) neutrons probe the nuclear density, i.e. they are not disturbed by additional purely electronic changes of the investigated system, (iii) the scattering lengths of nitrogen (9.36 fm) and oxygen (5.803 fm) differ significantly, (iv) neutrons are sensitive to light atoms such as hydrogen, (v) the differing scattering lengths of isotopes can be exploited to investigate specific problems, and (vi) light-induced magnetic ordering can be probed.

A common problem in all photocryystallographic experiments (X-ray or neutron or electron diffraction) is the fact that only a fraction of the molecules (or sample) can be transferred to the excited or metastable configuration, such that one deals with a mixed system of ground state and excited/metastable state in the diffraction experiment. In an improved photocryystallographic setup one needs to determine the amount of excited species in order to exclude this parameter from the refinement.

In the following we describe the state-of-the art in neutron photocryystallography, which we achieved after many improvements of the technique such that now it is available to users worldwide at SINQ. The method, the necessary equipment and data treatment as well as the optical calibration experiments to determine the population of excited species is presented on the example of SNP, where neutron diffraction gives direct evidence for the nitrosyl linkage-isomers.

2. Neutron photocryystallography

2.1 The method

Experiments have been performed in four steps: (1) The characterization of the optical properties, (2) the measurement of the ground state on the neutron single crystal diffractometer, (3) the in-situ illumination of the crystal and (4) the collection of the neutron data set of the mixed system ground/metastable state. For SNP, we performed such measurements for the two metastable states, SI and SII.

The ground state data set is necessary as a reference (difference Fourier maps). Refinement has been done using JANA2000 [16], now available as JANA2006. The detailed results are described in separate publications (SI [15], SII [14]). We discuss here the special details concerning photocryystallography, e.g. the refinement of mixed states (GS/SI and GS/SII with partial populations $P_3$) with necessary restrictions as well as the results from the support measurements such as absorption $a$ used in order to reduce parameters and to increase the quality of our results. We also discuss in detail the relation between the optical absorption properties and the populations $P_r$.

2.2 The neutron diffractometer TriCS

The neutron diffraction experiments on the metastable linkage isomers in SNP were performed on the single-crystal diffractometer TriCS [17], which is located at the Swiss Spallation Neutron Source SINQ [18] at PSI/Villigen. TriCS is a dedicated single crystal neutron diffractometer equipped with 1 single detector and 2 area detectors of 160 by 160 mm$^2$ active area. The detectors are separated by 45° in 2θ, and individually tiltable +30/−10°. Two focusing monochromators are available: Ge$_{311}$ delivering a wavelength of 1.180 Å and C$_{502}$ delivering 2.318 Å. The maximum flux reached for 1.180 Å at the sample position of the instrument was 1.04·10$^6$ n/cm$^2$/s using Megapie [19], a liquid Pb/Bi target, and a continuous proton beam of 1.35 mA/0.8 MW on target.

The sample environment of the single crystal instrument TriCS at the Swiss spallation neutron source SINQ has been modified in order to allow in-situ illuminations with up to 200 mW/cm$^2$ in the wavelength range from 400 to 800 nm on the instrument directly before the collection of the datasets at temperatures down to 20 K, depending on the heat conductivity of the sample. Other wavelength ranges can be realized by exchanging the light source or installing external user equipment.

2.3 Sample preparation and illumination

In order to investigate the metastable nitrosyl linkage-isomers by static photocryystallography the samples need to be cooled below ~100 K [6]. We therefore installed a closed cycle cooling machine schematically shown in Fig. 2, which delivers 10 K under standard operation. As we are using open heat shields to have access with light, but also due to the absorbed light during the illumination process, the lower limit is between 20 K and 30 K for photocryystallographic applications. During the measurement, the sample has to be kept under vacuum. Many sample such as SNP are not stable under vacuum at room temperature as they contain crystal water. We overcome this limit by undercooling the sample down to approximately 250 K, before applying the insulating vacuum. In earlier data collections, both X-ray [11] and neutrons [6, 20, 21], the population number reached for the metastable state was always a matter of debate. As a consequence, we have chosen in the latest experiments an in-situ illumination process directly on the instrument, which allows us to monitor the population number with the same light as used for the population of the metastable states. This has been reached by installing a fiber optic beyond the crystal as indicated in Figs. 2 and 3. This method allows us to measure the transmitted light outside of the closed cycle refrigerator and hence to determine the population of the metastable states with high accuracy.

We cut the SNP crystals normally perpendicular to the orthorhombic a-axis to plates with a thickness about $d = 0.05$ cm a diameter of 0.7 cm. This is a compromise between resolution, population and intensity: Too big crystals lower the resolution significantly, too thick crystals do not allow a homogenous population, and too small crystals lower the intensity of the neutron signal and limit the reliability of the measurement as discussed later in the simulations used for planning the experiments. A flat crystal close to the maximum diameter (limited by a homogenous illumination of the neutron beam) has been chosen according to these constraints. The temperature is kept constant around 50(2) K during data collection. Illumination of the crystal was performed using a Xenon lamp and a set of...
filters, as indicated in Fig. 3. Filtering the light was reached in several steps: H2O filter to remove the infrared light, broad band filter F1 to shorten the wavelength band and remove the major part of the unwanted radiation, interference filter F2 for a first selection of the illumination band and the final interference filter F3 to give a narrow wavelength band before polarizing the blue light along the c-axis of the crystal, the most efficient direction for population as the c-axis is perpendicular to all NO-bonds in the case of SNP. The total exposure was about 5000 J/cm² using an average power of only 20 mW/cm². It is known from wavelength-dependent differential scanning calorimetry (DSC) measurements [22] that illumination in the spectral range of 430 to 470 nm with polarization along the c-axis of the crystal yields a SI population of about 45–50% and a SII population of about 3–5%.

In order to obtain a high population of SII the following procedure has been proven to be most adequate: First the state SI is produced using light in the blue-green spectral range as described above. Then SI is transferred to SII using infrared light [22]. Using the wavelength 1064 nm, about 60% of the SI population is transferred to SII, while the remaining decay back into the ground state, such that SII populations above 20% can be reached by this procedure [25]. The transfer can be monitored by recording the transmitted light intensity of the infrared light. In this manner the population of SII can be determined from the transmission measurement as done in Ref. [14], where 16% of SI were reached.

2.4 From optical absorption to population

In SNP, the generation of the metastable linkage isomers is connected with optical absorption changes, which are known from low-temperature absorption spectroscopy [25]. Therefore the change of the transmitted light intensity during illumination can be used to determine the population numbers of the metastable states, SI and SII. For new systems the absorption curves would have to be determined first.

The used photocystallographic setup of TrICs@SINQ allows for the in situ measurement of the optical absorption with a Silicon photodiode as described above. In order to have a well-defined signal, the transmitted light was narrowed by an interference filter at 458 nm with a narrow transmission band (full width at half maximum of 2 nm). The detected time-dependent photovoltage \( U(t) \) can be described by

\[
U(t) = a \cdot I(t) = a \cdot I_0 \cdot e^{-\alpha(t) \cdot d}
\]

where \( \alpha \) denotes the absorption coefficient, \( d \) the crystal thickness, and \( I_0 \) the constant incident light intensity. \( \alpha \) is a proportionality constant, describing the detection efficiency of the diode. During illumination the absorption changes as a function of exposure \( Q = I_0 \cdot t \), where \( t \) is the time, due to the change in population of the three involved states GS, SI, and SII. Hence the total absorption coefficient is given as the sum of the single contributions

\[
\alpha(t) = \alpha_{GS} \cdot P_{GS}(t) + \alpha_{SI} \cdot P_{SI}(t) + \alpha_{SII} \cdot P_{SII}(t)
\]

where \( P_{GS,SI,SII} \) denote the populations of the different states GS, SI and SII respectively. It is known from the
At the beginning of illumination all molecules are in the saturation population of SI and SII respectively. Fitting the nation scheme in Fig. 2. Since we know the absorption values \( a \) for SI and SII (in our case 40% for SI and 4% for SII [15]), in good agreement with absorption, infrared, and Fe-Mössbauer measurements such as Raman (Ref. [23] for SNP or [24] for \( K_2[RuCl_3]NO \)). In the case of neutron diffraction measurements are not possible. The results shown in Fig. 5. Measurement of the population of SI in Sodiumnitroprusside (SNP) using neutron diffraction on Morpheus (former name: TOPSI). The values are in excellent agreement with the other methods used on TriCS (light absorption, [13]) and D9 (illumination time estimated from previous Mössbauer measurements [6]).

### 2.5 Population determination by neutron diffraction: an alternative for special cases

As an alternative option for the determination of the population of the metastable states, direct measurements of the neutron form factor, \( F \), of a reflection sensitive to the structural changes can be done. In the case of SNP, this is possible, as all structure factors are real (space group \( Pnma \)), a fact which has been already used by others to calibrate time-dependent intensities in the case of the decaying metastable states measured with X-rays [11]. Thereby the structure factor is given by

\[
F = n \cdot F_{GS} + (1 - n) \cdot F_{MS} = n \cdot F,
\]

where \( n \) is the population of the metastable species.

Figure 5 shows the results obtained on the reflection (107) for SNP which was calibrated against the optical absorption. The structure factors and the assumed population of earlier neutron diffraction measurements are indicated showing rather good agreement.

The disadvantage of this method is, that the reflections have to be selected by results not measured yet, but just predicted by theoretical calculations such as DFT (for SNP, e.g. [12]) or by assumption from spectroscopic measurements such as Raman (Ref. [23] for SNP or [24] for \( K_2[RuCl_3]NO \)). In the case of neutrons, extinction as a result of the heat load from the illumination may influence the results. Furthermore the error is linear in the population \( n \) (see Eq. (10)). As a consequence, we used for the determination of the population in the case of SNP optical absorption measurements rather than this method. However, this method can be an alternative if optical absorption measurements are not possible. The results shown in
2.6 Structure refinement of SI and SII in SNP

Also in SNP – as in all other systems known up to date – only a limited population of the metastable states has been achieved. As a consequence, the refinement of the two data sets (SI and SII) had to be done on a mixed system of the ground state and at least one metastable state as explained above. From our absorption measurement [25], we know the population of the crystal after the illumination. In the case of the SI-data-set the values were determined to be 4% of the NO ligands in the SII position, 40% in the SI position, and 56% in GS [15], for SII-data set 16% in SII and 84% in GS [14]. We also measured a data set of the pure ground state (GS) for reference. The refinement package used was JANA2000 [16]. In a first step, difference Fourier maps between the ground state structure and the observed data sets SI and SII (photo difference Fourier maps) were calculated. The difference is a result of the photoinduced states. They easily give the location of the atoms involved in the structural change. In a second step we performed a refinement with part of the molecule in a structurally different metastable state. Such a refinement is limited by assumptions e.g. that the central Fe atom or the CN-ligands are not involved in the structural change and stay unchanged. It is therefore important to watch temperature factors as wrong assumption may be covered by such corrections.

The structure factor $F$ for any hkl can be written as a function of the structure factors of the ground states GS and the metastable state S (where S is SI or SII):

$$F = (1 - n_S) F_{GS} + n_S F_S = F_{GS} - n_S \cdot \Delta F$$

with

$$\Delta F = F_{GS} - F_S .$$

In the special case of SNP with space group $Pnma$, all structure factors are real, and we can write

$$F(t) = \sqrt{I_0(t)} .$$

For X-ray diffraction, the destruction of the metastable states as a function of time ($t$) has to be taken into account. This can be done by describing the population $n_S(t)$ ($S = SI, SII$) as

$$n_S(t) = n_{SI} \cdot e^{-\gamma \cdot t},$$

as done successfully by Carducci et al. [11], however, complicating the refinement further. Due to the lower energy of the probing neutron, $n_S$ is constant for neutron diffraction.

2.7 Simulations of photocrystallographic Fourier maps using JANA2000

In photocrystallography, we are mostly faced to the measurement of mixed states, as a full population can not be reached due to internal limits of the system. Planning the measurement is therefore an essential step. We therefore introduced a simulation mode into JANA2000 (as well as the successor JANA2006) and have tested it successfully on the example of SNP. As our main goals are the photo Fourier maps in the most interesting plane involving the NO molecules, we tested them on the example of SII for three parameters which can vary in the experiment: population of the metastable states SII, coverage of the $q$-range (max $\sin(\Theta) / \lambda$ we measure) and statistics (represented by $s$). $s$ can be influenced by introducing artificial noise to the data. Figure 6 shows the different plots illustrating the expected visibility of the side-on configuration of the NO-bond in SII (horizontal NO-bond in the figures) in the presence of the ground state GS (vertical NO-bond in the figure). The results are obvious: The increase of the $q$-range $\sin(\Theta) / \lambda$ from 0.4 Å$^{-1}$ to 0.7 Å$^{-1}$ is increasing the quality.

Fig. 5 show excellent agreement between the two methods in the case of SNP.
of the data significantly more than increasing the population from 10% to 20%, whereas increasing the statistics has a lower influence. In consequence, we made a measurement on a 20% populated crystal covering 0.7 Å⁻¹ in sin (θ)/λ on a thin crystal, therefore limiting our counting statistics in order to reach an optimal result. The method successfully applied to SNP can be used for any system, also to standard systems containing only one molecule. In our case, increasing the coverage of sin (θ)/λ from 0.4 Å⁻¹ to 0.7 Å⁻¹ elevates the number of reflections to be collected by a factor of 4.4 (SNP, λ = 1.18 Å), similar to the factor of 4 needed to reduce the statistical error from 6 s to 3 s, but the increase in the q-range is significantly more improving the Fourier maps as is shown by Fig. 6.

3. Conclusions

The neutron diffraction experiments on the metastable excited states SI and SII of Sodium nitroprusside (SNP, Na₂[Fe(CN)₅NO]·2H₂O) using neutron single crystal diffraction show the improvement reached in photocryocrystallography within the last decade. The in-situ determination of the population of the metastable states by measuring absorption of the illuminating light considerably improved the reliability of the experiments since this important parameter is eliminated from the refinement and replaced by a directly measured value. The simulation of photo difference Fourier maps with JANA2006 [16] allows to determine the conditions for a successful experiment such as the required q-range and minimum population as well as the measurement statistics to reach desired error (σ) for the diffraction data sets.

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