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Photoinduced Nitrosyl Linkage Isomers Uncover a Variety of Unconventional Photorefractive Media**

By Dominik Schaniel,* Mirco Imlau, Thomas Weisemoeller, Theo Woike, Karl W. Krämer, and Hans-Ulrich Güdel

The ongoing search for new photorefractive materials offering a high photosensitive flexibility is triggered by the limited tuning ability of conventional photorefractive materials, such as electro-optic crystals, photopolymers, or liquid crystals. One of the latest discovered photorefractive materials is $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, in which metastable linkage isomers of the nitrosyl group can be generated by light irradiation resulting in huge changes of the refractive index up to $\Delta n \sim 10^{-2}$. Here we show that this type of photorefraction is a general property arising from the generation of linkage isomers and can thus be found in many compounds containing $[\text{ML}_5\text{NO}]^{m\pm}$ complexes, where M is a transition metal, L a ligand, and m the formal charge of the anion/cation. The benefit of this generality is reflected in the tailoring properties of the photorefractive response such as the spectral sensitivity simply by selecting different representatives of the $[\text{ML}_5\text{NO}]^{m\pm}$ compounds.

Conventional photorefractive materials,^[1] where the light-induced modulation of the refractive index is caused by the linear electro-optic effect (Pockels effect), are widely applied in nonlinear optics.^[2] They feature reversible photorefractivity without chemical processing allowing for dynamical holography,^[3] and the kinetics of hologram formation is described by the well-known Kiev equations.^[4] In recent years a second class of reversible photorefractive media for dynamical holography has been established, the unconventional photorefractive materials. Here an optical bistability is at the origin of photorefraction and the kinetics show a characteristic transient behavior.^[5] The unique properties of this class were com-

prehensively investigated for the nitrosyl compounds $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (SNP) and $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$,^[6–8] where light irradiation induces a rotation of the NO ligand by 180° in the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complexes,^[9] as illustrated in Figure 1. This photoinduced linkage isomerism modifies the polarizability of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complex resulting in a macroscopic change of the single-crystal refractive index according to the Lorentz–Lorenz equation.

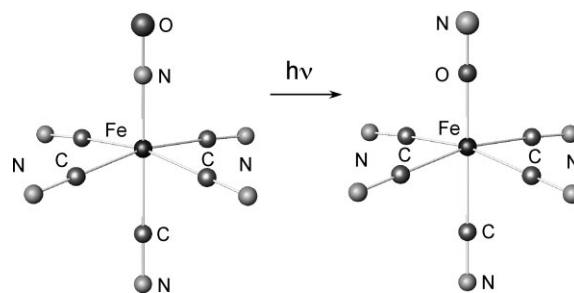


Figure 1. Light-induced linkage isomers of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complex [9].

Remarkably, SNP belongs to a family of compounds described by the general formula $\text{X}[\text{ML}_5\text{NO}] \cdot y\text{H}_2\text{O}$, with various central atoms $\text{M} = \text{Fe}, \text{Ru}, \text{Os}, \text{Ni},$ or Mo ; ligands L, for example, $\text{L} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{OH}^-, \text{CN}^-, \text{NH}_3,$ or $\text{C}_2\text{O}_4^{2-}$; counter ions $\text{X} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Cl}^-, \text{Br}^-, \text{NH}_4^+,$ or CN_3H_6^+ , and different amounts of crystal water y .^[10–13] In all these compounds light-induced linkage isomers of the NO ligand can be accessed by a metal-to-NO charge-transfer transition. Hence it can be suggested that any representative potentially shows photorefraction and that it belongs to the class of unconventional photorefractive materials.

To prove the general relation between photoinduced linkage isomers and the appearance of photorefraction, we focus on two further representatives of nitrosyl-containing complexes, namely $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$, in which all constituents but the NO ligand are exchanged compared to $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ and $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$. These two particular compounds were selected for their different complex charges, $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ being a cation and $[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]^{2-}$ being an anion. Thus we have the possibility to strictly relate any optical response to the NO–metal moiety of the compound

[*] Dr. D. Schaniel,^[†] Dr. M. Imlau, T. Weisemoeller
Fachbereich Physik, Universität Osnabrück
Barbarastrasse 7, 49069 Osnabrück (Germany)
E-mail: dominik.schaniel@uni-koeln.de

Dr. T. Woike
Institut für Mineralogie, Universität zu Köln
Zùlpicherstr. 49b, 50674 Köln (Germany)

Dr. K. W. Krämer, Prof. H.-U. Güdel
Department of Chemistry and Biochemistry, University of Bern
Freiestr. 3, 3000 Bern 9 (Switzerland)

[†] Current address: Institut für Mineralogie & Geochemie, Universität zu Köln, Zùlpicherstrasse 49b, 50674 Köln, Germany.

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independent of the chosen ligands and the charge of the complex.

Holographic light scattering was chosen as a simple tool to prove the photorefraction concomitant with the generation of the linkage isomers in the two substances.^[14] We find that photorefraction is independent of any specific ligand or cation/anion, so that we establish photorefraction as a general property resulting from the photoinduced nitrosyl-linkage isomers in this substance class.

First we prove that $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$ are photorefractive, that is, light exposure causes a change of the refractive index. For this purpose single crystals of the two representatives were exposed to an unexpanded coherent laser beam (wavelength, $\lambda = 458 \text{ nm}$). Around the directly transmitted pump beam a radially symmetrical intensity distribution (external apex angles $\theta_{x,y}$), called corona,^[14] built up as a function of exposure at low temperatures ($T = 100 \text{ K}$) for $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (Fig. 2a) and for $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$ (Fig. 2b).

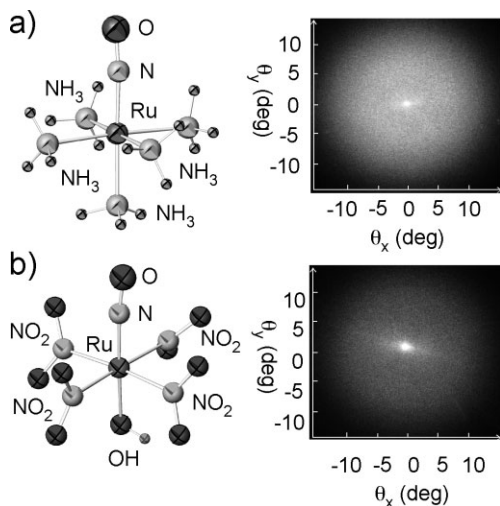


Figure 2. a) $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ complex (left) and scattering corona observed in a c-cut (crystal plane cut perpendicularly to the c-axis with thickness d) of $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ after illumination with $\lambda = 458 \text{ nm}$ ($Q = 2000 \text{ J cm}^{-2}$, $\mathbf{E} \parallel \mathbf{b}$, $\mathbf{k} \parallel \mathbf{c}$) (right). b) $[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]^{2-}$ complex (left) and scattering corona observed in a b-cut of $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$ after illumination with wavelength $\lambda = 458 \text{ nm}$ ($Q = 3000 \text{ J cm}^{-2}$, $\mathbf{E} \parallel \mathbf{c}$, $\mathbf{k} \parallel \mathbf{b}$). The temperature of the measurements was $T = 100 \text{ K}$.

The corona resulted from pump-beam diffraction at a photoinduced refractive-index modulation $n(\mathbf{r})$. At the beginning of exposure, the incoming pump beam was scattered at imperfections in the crystal or on its surface. Consequently, a multitude of weak scattered waves were present in the crystal bulk as well as the strong pump beam. Interference between the scattered waves and the pump beam yielded a light interference pattern $I(r)$, which can be regarded as a superposition of sinusoidal light-intensity modulations with periodicity A_i ($i = 1, \dots, N$). In a photorefractive crystal with average refractive index n_o , any sinusoidal intensity modulation will be trans-

ferred into a sinusoidal modulation of the refractive index $n_i(\mathbf{r}) = n_o + \Delta n_i(\mathbf{r}) \cos(2\pi \mathbf{r}/A_i)$, which acts as a volume diffraction grating for the pump beam. The pump-beam diffraction yielded a wave in the direction of the scattered wave, that is, the wave front of the scattered wave was reconstructed by the grating in accordance with the fundamental holographic principle introduced by Gabor.^[15] Therefore, the entire process of pump-beam diffraction at photoinduced refractive index modulations is known as holographic light scattering. The initially weak scattered intensity is amplified up to a saturation value via beam-coupling processes or, as shown for SNP,^[7] via the nonlinear photorefractive response.

As in any other diffraction process, the diffraction at the recorded volume grating $n_i(\mathbf{r})$ obeys Bragg's law. In the recording geometry, the pump beam automatically fulfilled the Bragg condition of any grating $n_i(\mathbf{r})$. As a result the pump beam was diffracted comprehensively, which led to the scattering corona around the directly transmitted pump beam as observed for the two investigated samples (Fig. 2). In contrast, read-out of the gratings with an angular or wavelength-detuned pump beam inevitably led to a mismatch of the Bragg condition for a majority of gratings such that the corona vanishes. Nevertheless, a modified scattering pattern remained, resulting from the particular gratings still obeying the Bragg condition. For an angular detuning, such gratings constitute a cone of diffracted waves in accordance with the Ewald-sphere concept.^[16] Projected on a screen behind the sample the cone appears as a bright ring as shown in Figure 3 exemplarily for $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ at $T = 100 \text{ K}$. The vertical line can be explained by the Ewald-sphere concept as well, and belongs to the diffraction cone of the primary image with a comparably large apex angle.



Figure 3. The scattering corona changed to a scattering cone, when the pump beam read out the written refractive index gratings under the angle θ . The picture shows the projection of the holographic scattering cone on a screen behind the sample, a c-cut of $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (thickness $d = 0.24 \text{ mm}$), after illumination with 458 nm ($Q = 500 \text{ J cm}^{-2}$, $\mathbf{E} \parallel \mathbf{a}$, $\mathbf{k} \parallel \mathbf{c}$) for a read-out angle of $\theta = 6^\circ$ at $T = 100 \text{ K}$.

The process of holographic light scattering inevitably requires the presence of a photorefractive response. Thus the appearance of the corona upon exposure and of the conical light scattering upon angular detuning are convincing proof of the presence of photorefraction in both investigated samples.

Second we prove the relation of the photorefractive response to the photoinduced linkage isomers. The scattering vanished with heating above 260 K and 190 K for $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$, respectively. This shows already that the phenomenon of holographic scattering is connected with the nitrosyl-linkage isomer, which indeed has a decay temperature of $T_M = 260 \text{ K}^{[17]}$ and $T_M = 190 \text{ K}^{[18]}$ for the two compounds, respectively. In addition, we investigated the kinetics for the build-up of the scattering at low temperature, as it is connected to the number density of photoinduced linkage isomers. Figure 4 shows the intensity of the directly transmitted beam together with the intensity of the corona measured at an apex angle $\delta = 7^\circ$ as a function of the

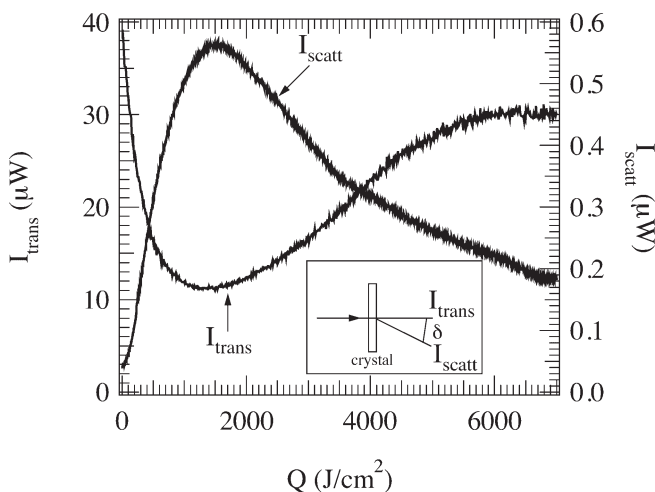


Figure 4. Intensities of the directly transmitted beam I_{trans} and of the scattering corona measured at an apex angle $\delta = 7^\circ$ (I_{scatt}) as a function of exposure Q (c-cut, $d = 0.17 \text{ mm}$, pump and read out wavelength $\lambda = 458 \text{ nm}$, $\mathbf{E} \parallel \mathbf{b}$, $\mathbf{k} \parallel \mathbf{c}$) in $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ at $T = 100 \text{ K}$.

exposure Q for $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$. The intensity of the corona increased with exposure. Upon passing the maximum at $Q = 1.2(1) \times 10^3 \text{ J cm}^{-2}$, it decreased and nearly vanished for large exposure. The inverse behavior of the transmitted pump beam simply reflected the energy conversion of the total transmitted light. Equivalent transient kinetics with exposure were obtained for $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$.

This remarkable transient behavior of the scattered light intensity is analogous to that found for SNP,^[14] and has been successfully described on the basis of an optically bistable photosensitive material consisting of the two configurations M–NO and M–ON.^[5] The scattering maximum represents the state where a spatial modulation of the number density of M–ON, that is, a spatial modulation of the refractive index change, reaches its maximum amplitude. This spatial modulation vanishes in an overexposed sample, where the number

density of molecules transferred to the isonitrosyl configuration M–ON is homogenous in the whole crystal. Hence the observed transient kinetics shows that holographic scattering is directly connected with the generation of the linkage isomers and that both selected representatives belong to the class of unconventional photorefractive materials.

Summarizing the experimental part, our results show that photorefraction appeared in the two compounds $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$, and that it was strictly related to photoinduced linkage isomers in analogy to the photorefractive response in SNP, that is, the light-induced linkage isomers are the cause of the photorefraction.^[7] Consequently the photorefractive response is local, that is, the refractive index modulation is in phase with the light intensity pattern, and huge refractive index modulations can be expected, for example, $\Delta n = 2 \times 10^{-2}$ in SNP.

By comparing our findings with the results reported for some $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ containing compounds,^[6–8,14] by analyzing the macroscopic photorefractive properties with respect to the microscopic changes in the metal–nitrosyl bonding, we obtain an exciting result: Photorefraction is a general property of the light-induced linkage isomers in $[\text{ML}_5\text{NO}]^{m\pm}$ compounds containing a nitrosyl ligand, independent of the metals M, the ligands L, or the charge m of the complex.

The implications of this conclusion are far reaching. It allows the exploitation of their peculiar properties^[12,13] in order to tune them for applications as is similarly done by doping or applying external fields in common oxidic electro-optic materials or polymers.^[1,2] The only necessary prerequisite is the existence of an optically accessible metal-to-NO charge-transfer transition. Tunable properties are the lifetime, the spectral range, and the size of the photorefractive response, which is proportional to the number density of photoinduced linkage isomers. Tuning parameters are the chemical composition, that is, the choice of ligands L, central atoms M, and counter ions X; and external parameters such as temperature, exposure time, and light polarization. The lifetime τ of the photoinduced linkage isomers can be changed over many decades, from $\tau = 46 \text{ s}$ for *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$,^[19] to $\tau = 1.8 \text{ s}$ for $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$,^[17] and $\tau = 3.9 \times 10^{-4} \text{ s}$ for SNP at 300 K. Additionally, τ can be varied from nearly infinite at low temperatures to very short times at high temperatures as the decay follows the Arrhenius law, for example, $6 \times 10^{19} \text{ s}$ at 100 K, and $5 \times 10^{-7} \text{ s}$ at 400 K for SNP. Therefore, one could use the same material for long-time storage at sufficiently low temperature and for fast optical switching or as saturable absorbers at elevated temperatures. The sensitive spectral range reaches from the near ultraviolet to the near infrared and can equally be selected by choosing appropriate compounds.^[12,20–22] Note that the photorefractive response is large, for example, up to $\Delta n \approx 10^{-2}$ in SNP.^[18] By comparing the observed scattered intensities in $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$ with that of SNP,^[14] we can estimate the refractive index change of the former ones to $\Delta n \approx 10^{-3}–10^{-4}$. The somewhat smaller effect is because of the used illumination wavelength of $\lambda = 458 \text{ nm}$, for which the

number of generated linkage isomers, and hence the refractive index change, is not maximal.^[17,18] The size of the photorefractive response is additionally tunable by choosing different light polarizations or different exposure times, as in this manner the number density of generated linkage isomers can be adjusted.^[19–21] Moreover it was found that the generation of the linkage isomers in SNP by pulsed illumination at room temperature is faster than nanoseconds.^[23] Therefore they can be used for time-resolved photorefractive applications such as ultrafast dynamical holography. Possibly the most remarkable property of this class of photorefractive compounds is the molecular origin of the photorefractive response, which even allows the use of solutions of nitrosyl compounds for applicative purposes, as demonstrated in the literature^[23]. Solutions are much cheaper and easier to produce than crystals and are currently intensively investigated in the field of optofluidics, where fluidic and optical components are combined to yield highly tunable devices.^[24,25] Furthermore it allows embedding of the photorefractive complexes in suitable matrices such as polymers or glasses in order to extend their application range.

We have successfully applied holographic light scattering for the verification of the photorefractive response in various nitrosyl compounds. Having said that, this scattering commonly constitutes a serious drawback for the applications of photorefractive media in nonlinear optics, as it worsens the signal-to-noise ratio.^[26] However, the scattering can be reduced considerably by preparing crystals of higher optical quality. Furthermore we would like to point out that—although holographic light scattering is present in SNP, too—the huge refractive index amplitude up to $\Delta n \sim 10^{-2}$ still enables an excellent signal-to-noise ratio for these nitrosyl compounds, qualifying them as suitable candidate materials for applications.^[7]

Experimental

Crystals of $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (space group *Pnma*) were grown from aqueous solution by slow cooling. A seed crystal was used and the temperature lowered from 70 °C to 30 °C with 1 K h⁻¹, typically. With an optical microscope the crystal quality was checked between crossed polarizers. The orientation of the crystal axes was determined by using X-ray diffraction. Single crystals of $\text{K}_2[\text{Ru}(\text{NO}_2)_4(\text{OH})\text{NO}]$ (space group *P2₁/a*) were grown and prepared as described elsewhere^[17].

The single crystals were cut perpendicular to the crystal axes to sizes 3 mm × 3 mm and thicknesses between 0.1 and 0.5 mm. They were polished with Cr₂O₃ to optical quality and mounted onto a sample holder diving into a nitrogen-filled dewar with four flat plane-parallel windows. The holographic scattering experiments were performed as described in the literature^[14], that is, the unexpanded beam of an argon-ion-laser ($\lambda = 458$ nm) struck the sample perpendicularly to the sample surface and the transmitted and scattered intensi-

ties were measured with Si-PIN diodes. Photographs were taken with a digital camera Canon EOS 10D.

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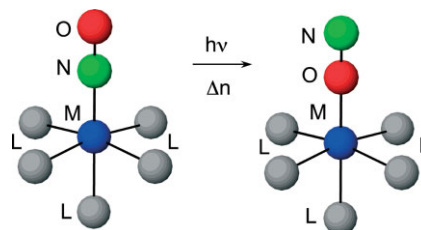
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COMMUNICATIONS

Photorefractive is shown to arise generally with the generation of light-induced linkage isomers in compounds containing the complexes $[ML_5NO]^{m\pm}$, where M is a transition metal, L a ligand, and m the formal charge of the anion/cation. The photorefractive properties of the complex can be tuned by chemical variation of M and L.



Optically Active Materials

D. Schaniel,* M. Imlau,
T. Weisemoeller, T. Woike,
K. W. Krämer, H.-U. Güdel ■ – ■

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