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Institute of Solid State Chemistry and Mechanochemistry

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Photo-reversibility and wavelength dependence of excited intermediates in nitro-nitrito linkage isomerization of $[Co(NH_3)_5NO_2]Cl(NO_3)$ crystals unveiled by photomechanical response

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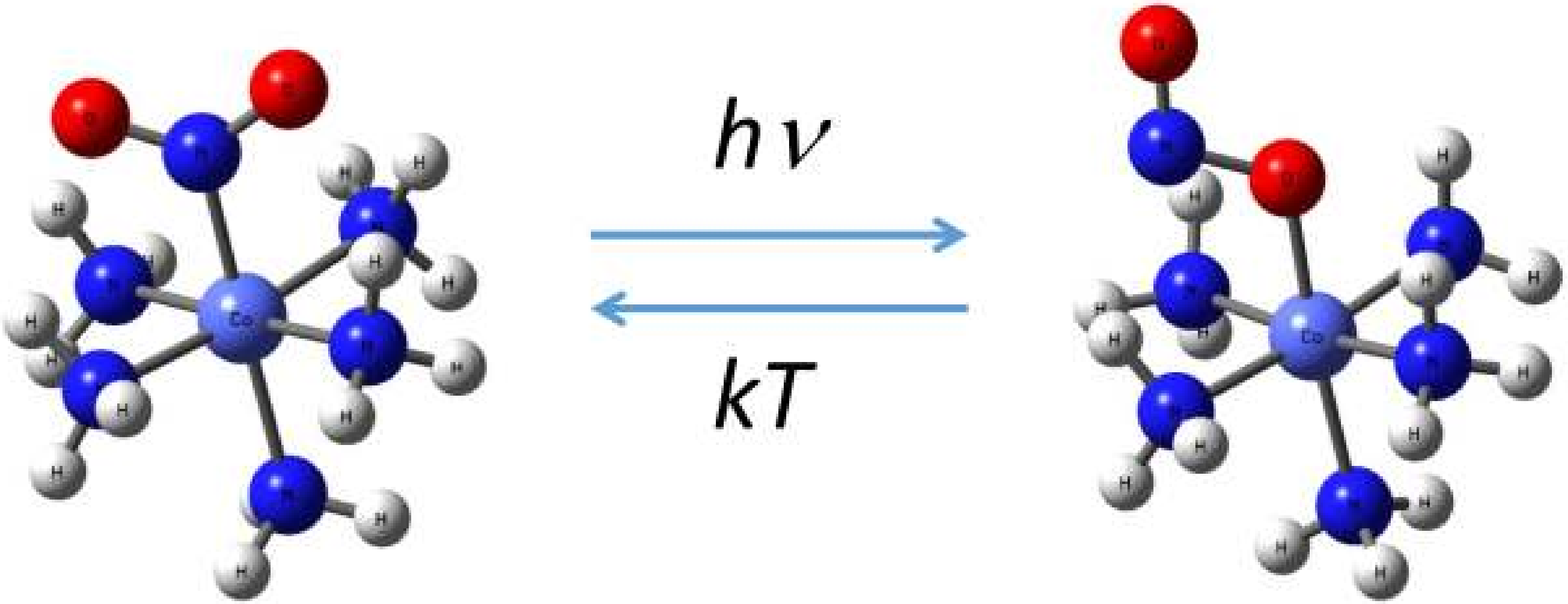
Linkage isomerism in $[Co(NH_3)_5NO_2]^{2+}$

$[Co(NH_3)_5\mathbf{NO_2}]^{2+}$ $[Co(NH_3)_5\textcolor{red}{\mathbf{ONO}}]^{2+}$



Gibbs & Genth 1856 ---> Jörgensen 1893 ---> Werner 1912 ---> Adell 1944---->....

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Reactions

Photolysis

Isomerisation

Solutions

Crystals and solutions

$^*Co(NH_3)_5NO_2^{2+} \rightarrow \{Co(NH_3)_5^{2+}, NO_2\}_{solvent\ cage}$

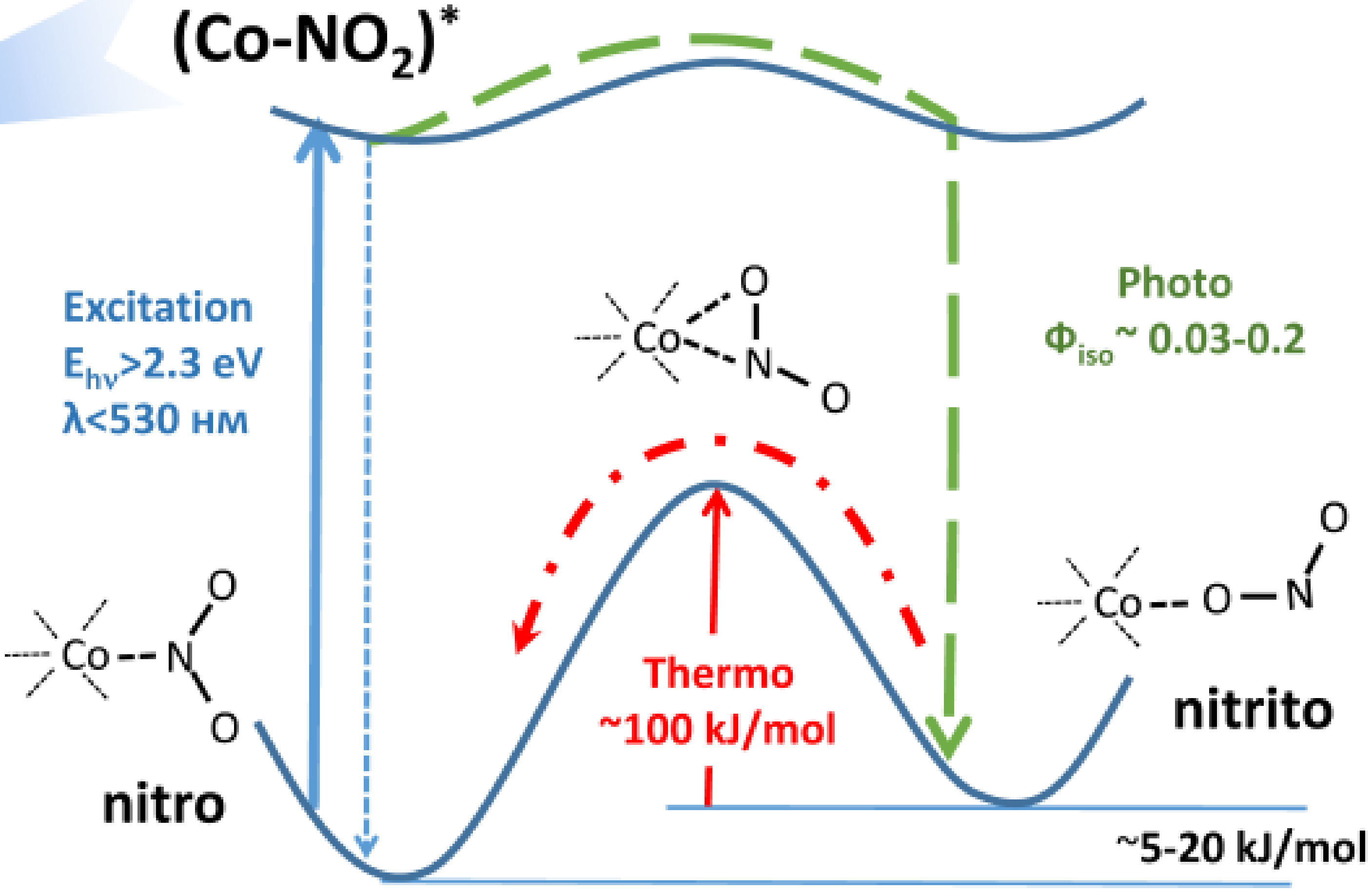
(bond homolysis in the reactive CT state)

$\{Co(NH_3)_5^{2+}, NO_2\}_{solvent\ cage} \rightarrow Co(NH_3)_5^{2+}, NO_2$

(diffusive cage escape)

$Co(NH_3)_5^{2+}, NO_2 \rightarrow Co^{2+} + 5NH_3 + NO_2$

(ultimate separation and decomposition)



Φ_{redox}~ 0.1-0.6

$\boxed{\Phi_{redox}/\Phi_{iso} = const \sim 3}$

V. Balzani, R. Ballardini, N. Sabbatini, L. Moggi, *Inorg. Chem.*, 1968, **7**

Early studies of photo-bending effect
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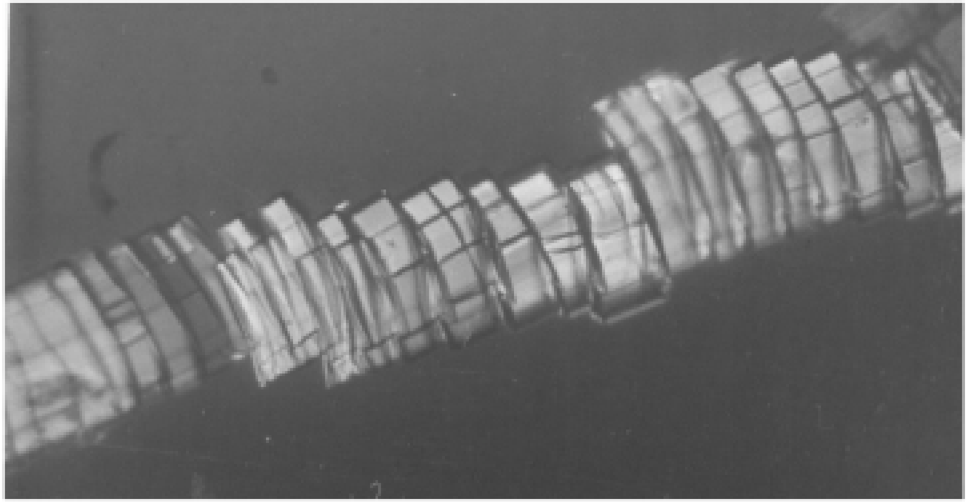
E. Boldyreva, A. Sidelnikov

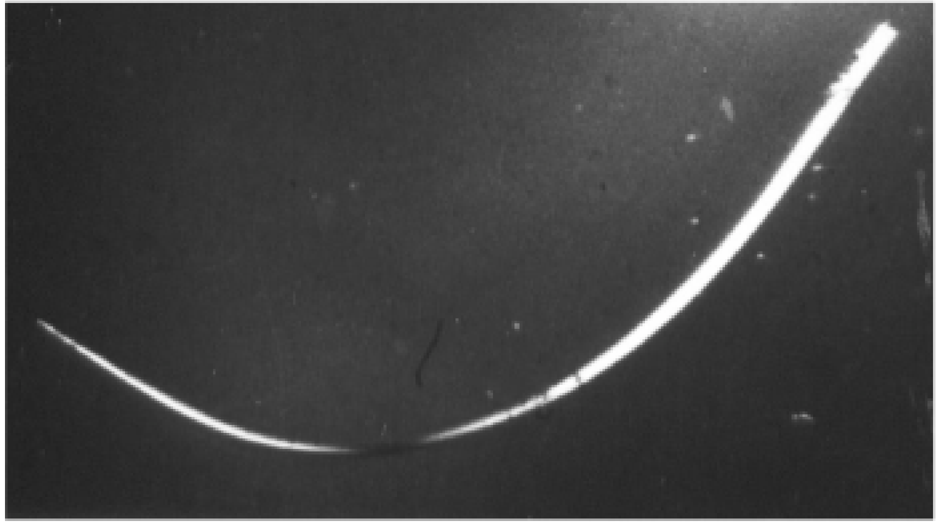
mid eighties

Photochemical isomerisation of needle crystals of $[Co(NH_3)_5NO_2]Cl(NO_3)$

…which they thought was $[Co(NH_3)_5NO_2]Cl_2$

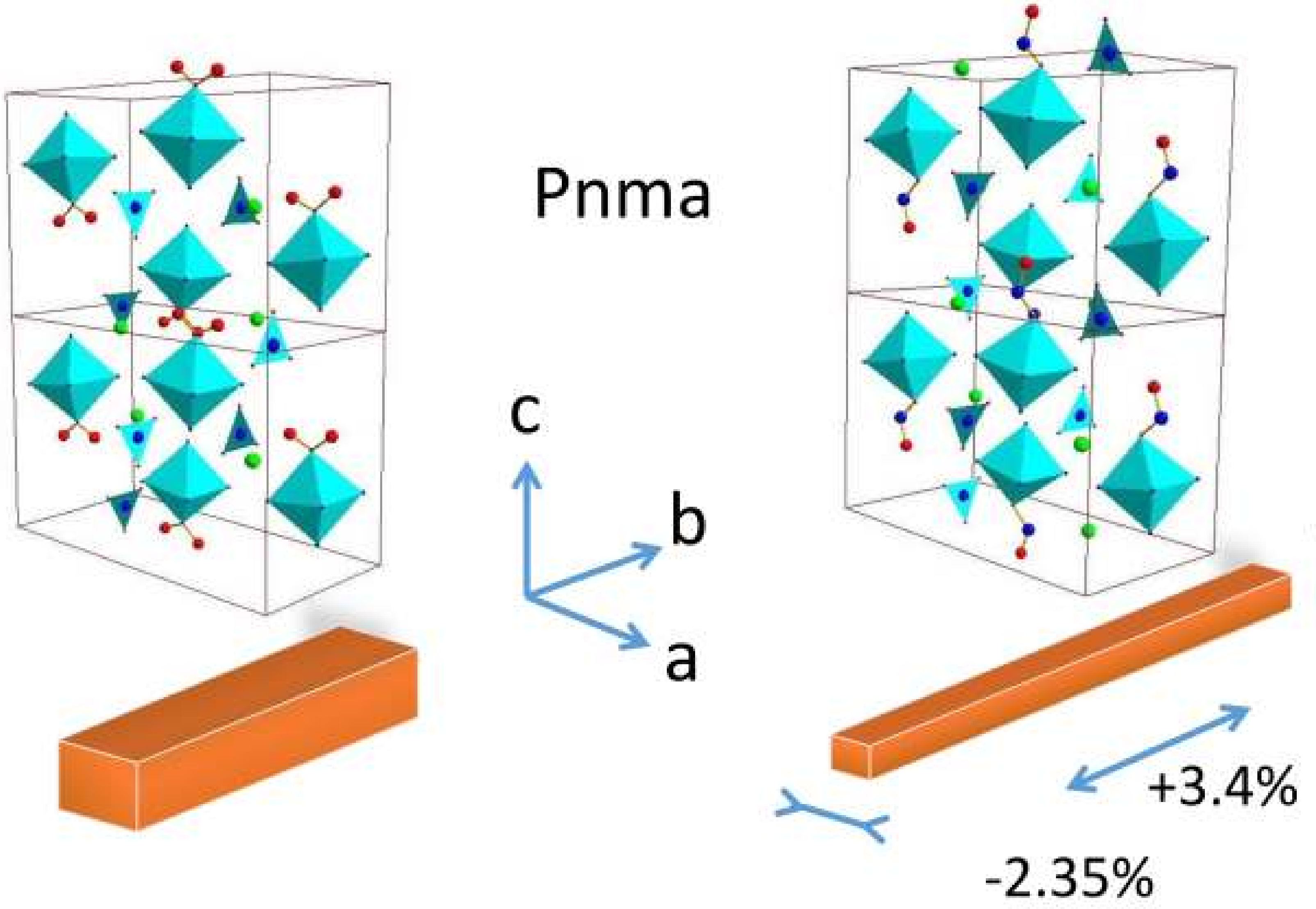


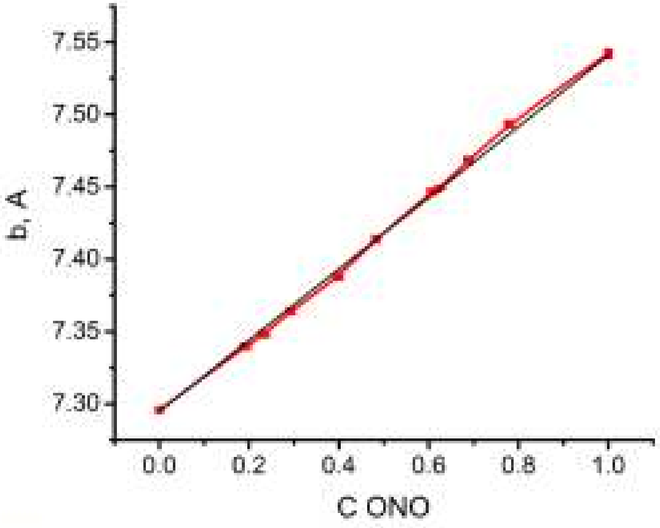
Crystals cracked after long irradiation if thicker than 50 µm



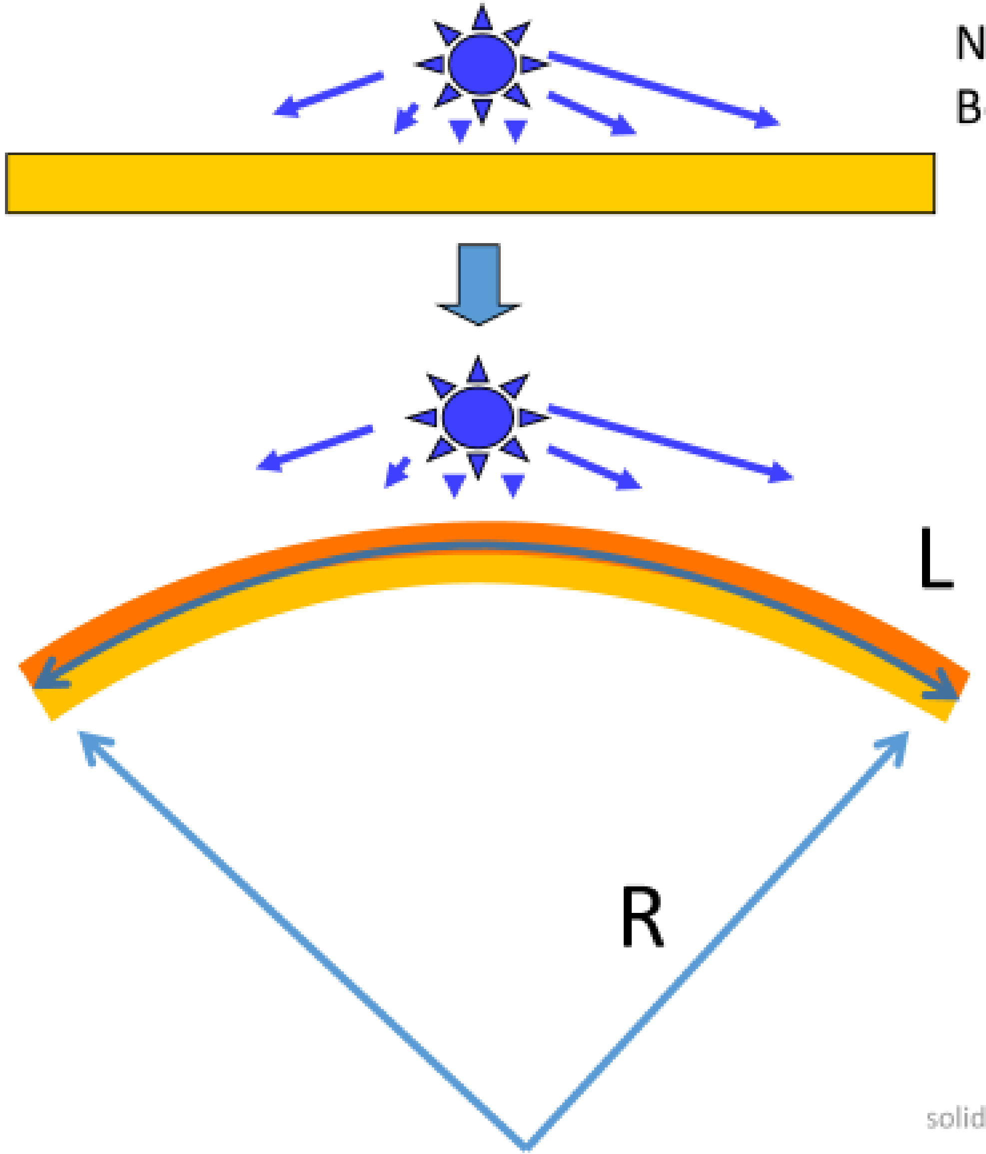
Thin crystals were reversibly bending and unbending

Change of structure parameters due to isomerization

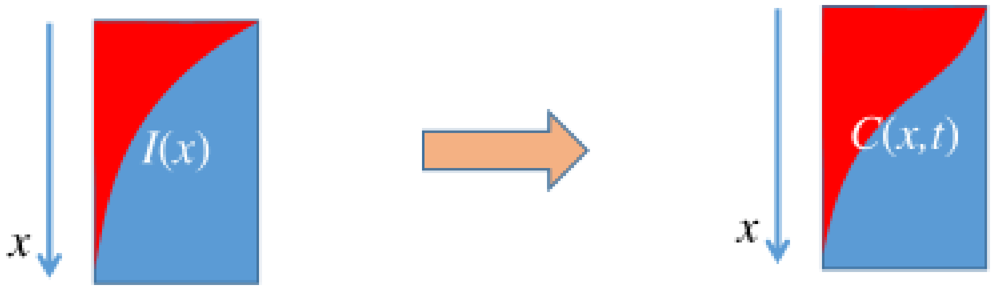




Crystal deformation due to photoisomerization (photomechanical response)



Non-uniform transformation occurs due to the absorption of light.
Bouguer-Lambert-Beer law



- longitudinal deformation (elongation)

$$\frac{\Delta L}{L}(t)=\frac{\varepsilon_0}{h}\int_0^h C(x,t)\,dx$$

- curvature

$$\frac{1}{R}(t)=-\frac{12\varepsilon_0}{h^3}\int_0^h\left(x-\frac{h}{2}\right)C(x,t)\,dx$$

E. Boldyreva, A. Sidelnikov
1987

? How will the initial bending speed of the crystal change if the reaction works against an external force?

! The external force leads to a noticeable decrease in the isomerization quantum yield.

External bending force resulting in only ~1% compression of the surface layer causes a 40% reduction in quantum yield. High sensitivity of the photochemical reaction to crystal strain!

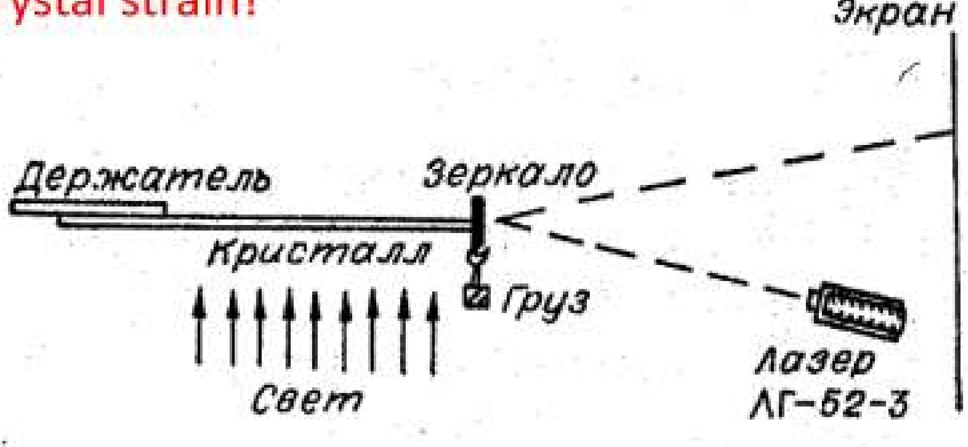
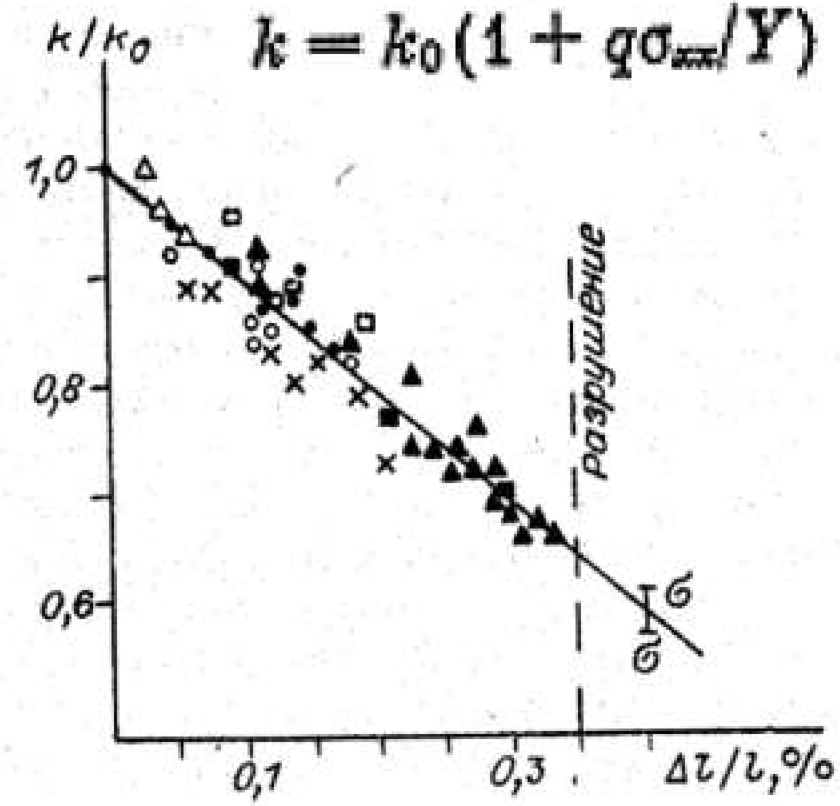
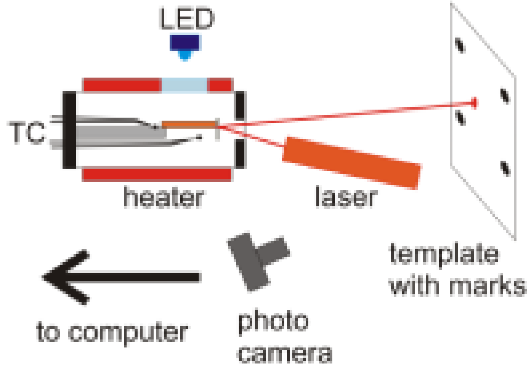


Рис. 1. Схема проведения эксперимента.

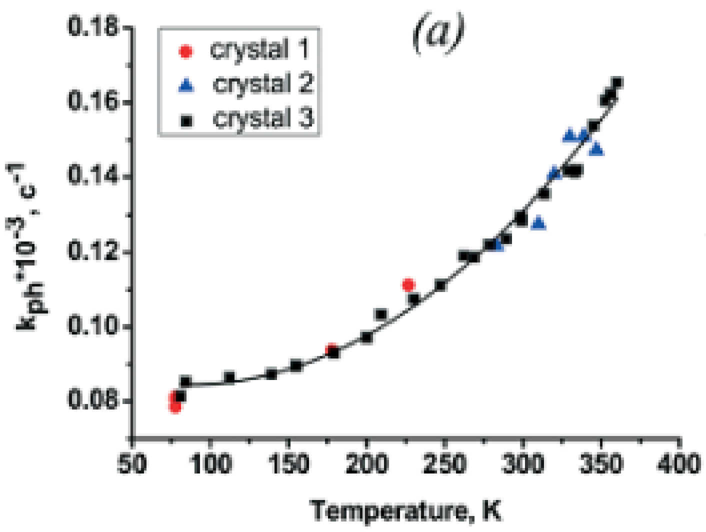


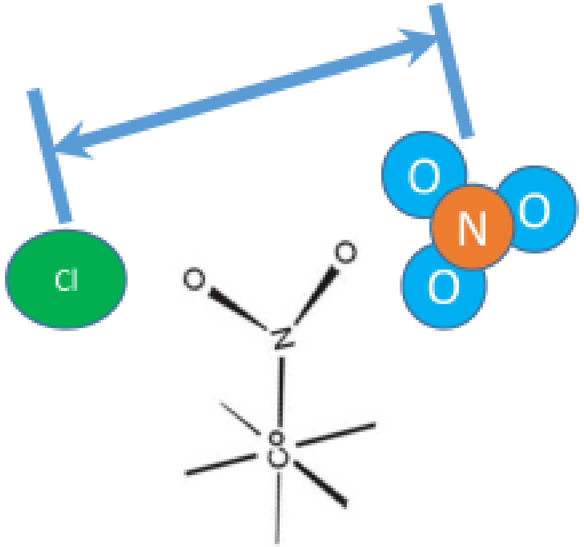
$$k = k_0(1 + q\sigma_{xx}/Y)$$

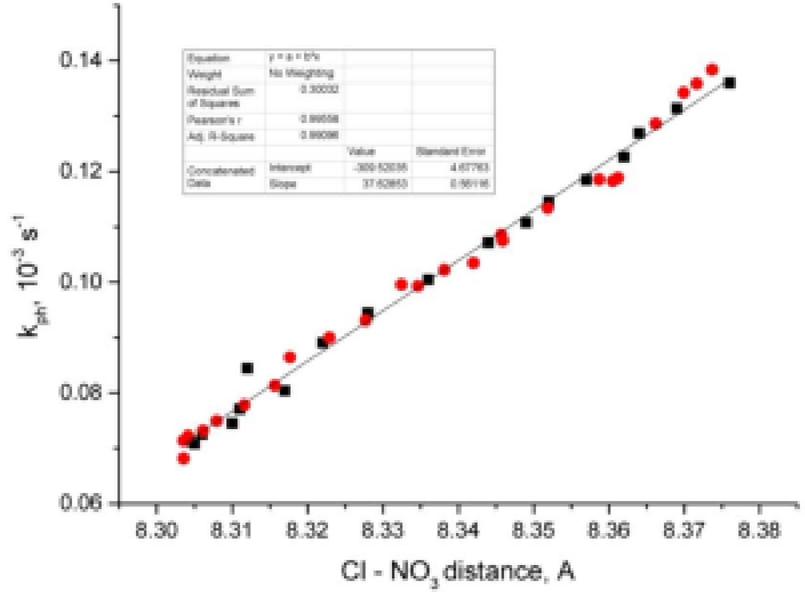
Photoisomerization quantum yield depends on structure deformation (environmental effect)



Effect of thermal expansion:





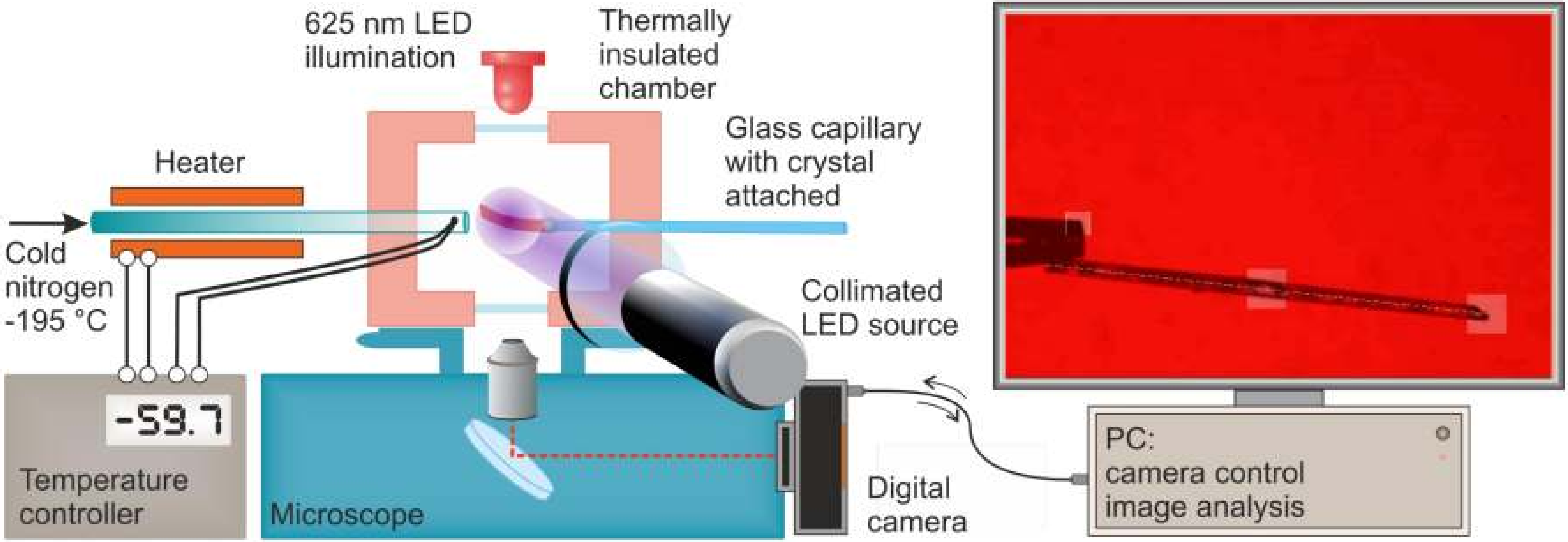


- Quantum yield decreases ~ twice on ~1% compression by external force
- Quantum yield decreases ~ twice on ~1% compression by thermal strain
- Then, the quantum yield should depend on the transformation itself as it causes stains ~1% - **feedback effect**

$$\frac{\Delta\Phi}{\Phi} \sim q_\sigma \varepsilon_\sigma + q_T \varepsilon_T + q_C \varepsilon_C = \mathbf{Q\varepsilon}$$

Measuring the mechanical response of thin crystals during transformation

- We can follow the entire kinetics of the conversion of nitro to nitrito, 0% to 100%.
- Sensitivity of the method to the transformation degree ΔC~0.1% (and ~0.01% for the cross-section gradient)
- We can study in-situ dependence of the quantum yield on the transformation at various wavelength and temperature.



Kinetic model

- Kinetic equation (photoisomerisation + thermoisomerization)

$$\frac{\partial C}{\partial t} = k_{\mathrm{ph}}\left(1 - C\right) - k_{\mathrm{th}} C$$

- Effective rate constant of photoisomerisation

$$k_{\mathrm{ph}} = I\left(x\right)\Phi\left(C\right)\frac{\mu_0}{C_0}$$

- Bouguer-Lambert-Beer law

$$I\left(x\right) = I_0 \exp\left\{-\int_0^x \left[\mu_0\left(1 - C\left(x'\right)\right) + \mu_1 C\left(x'\right)\right] dx'\right\}$$

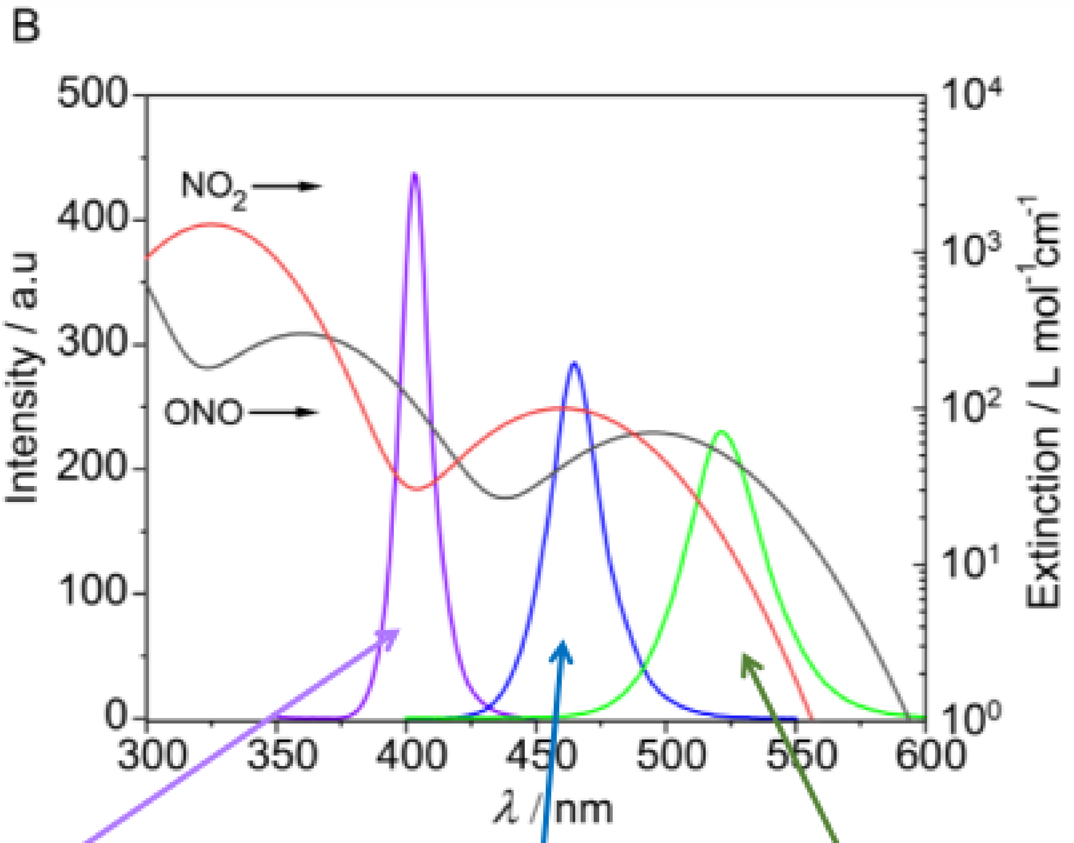
- Empirical dependence of the quantum yield of photoisomerization on the degree of conversion

$$\Phi\left(C\right) = \Phi_0\left(\lambda, T\right)\exp\left(q_C C\right)$$

Initial objectives of the study

1. Study of photoisomerisation kinetics in $[Co(NH_3)_5NO_2]ClNO_3$ crystals at various wavelengths and temperature

2. Modeling the transformation and determining the dependences of parameters on T и λ:
   - absorption coefficients of light by isomers
   - quantum yield of isomerisation
   - feedback coefficient



Violet 403±10 nm
Local minimum between 325 nm (CT) и 460 nm (d-d) bands

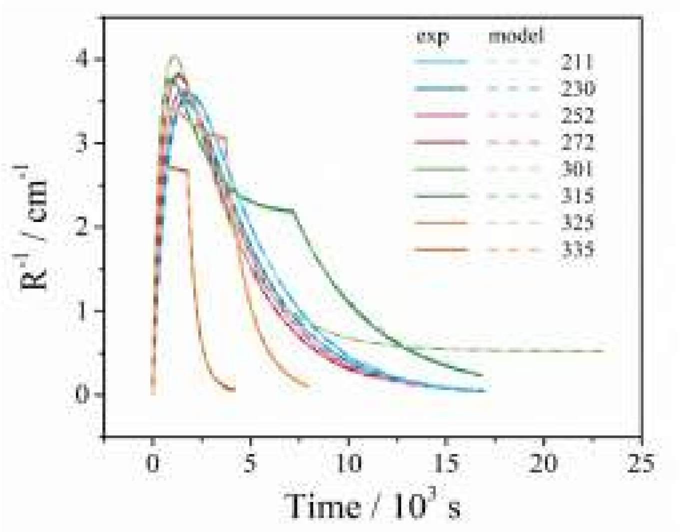
Blue 465±15 nm
Absorption maximum in visible light (460 nm, d-d band)

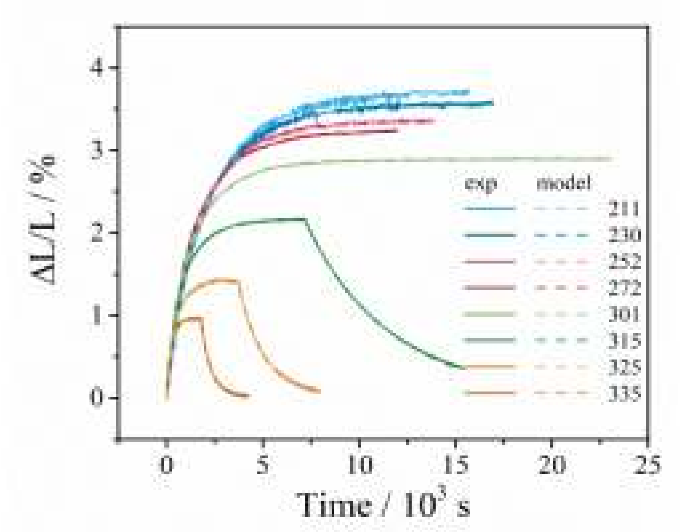
Green 523±20 nm
Low-energy edge of d-d band

The kinetics of mechanical response. Data and modelling

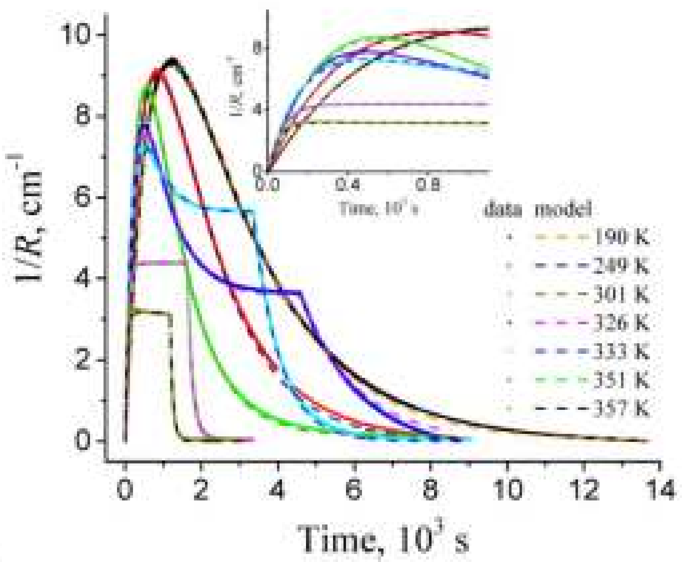
E. Ahmed, S. Chizhik, A. Sidelnikov, E. Boldyreva and P. Naumov, *Inorg. Chem.*, 2022, **61**, pp. 3573-3585.

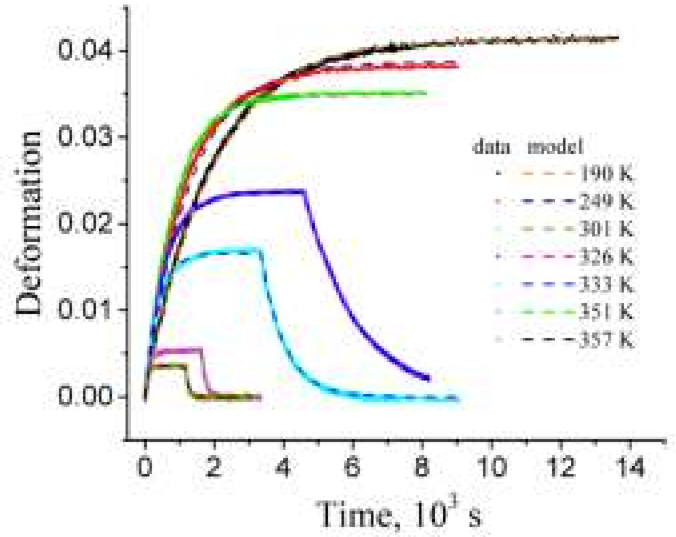
403 nm



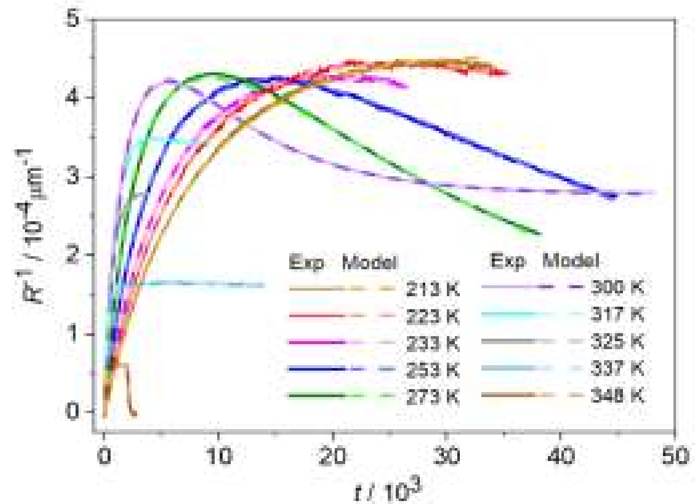


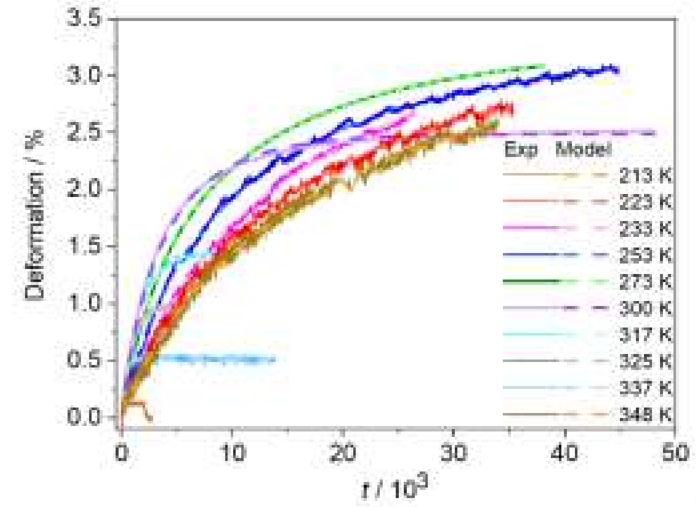
465 nm





523 nm





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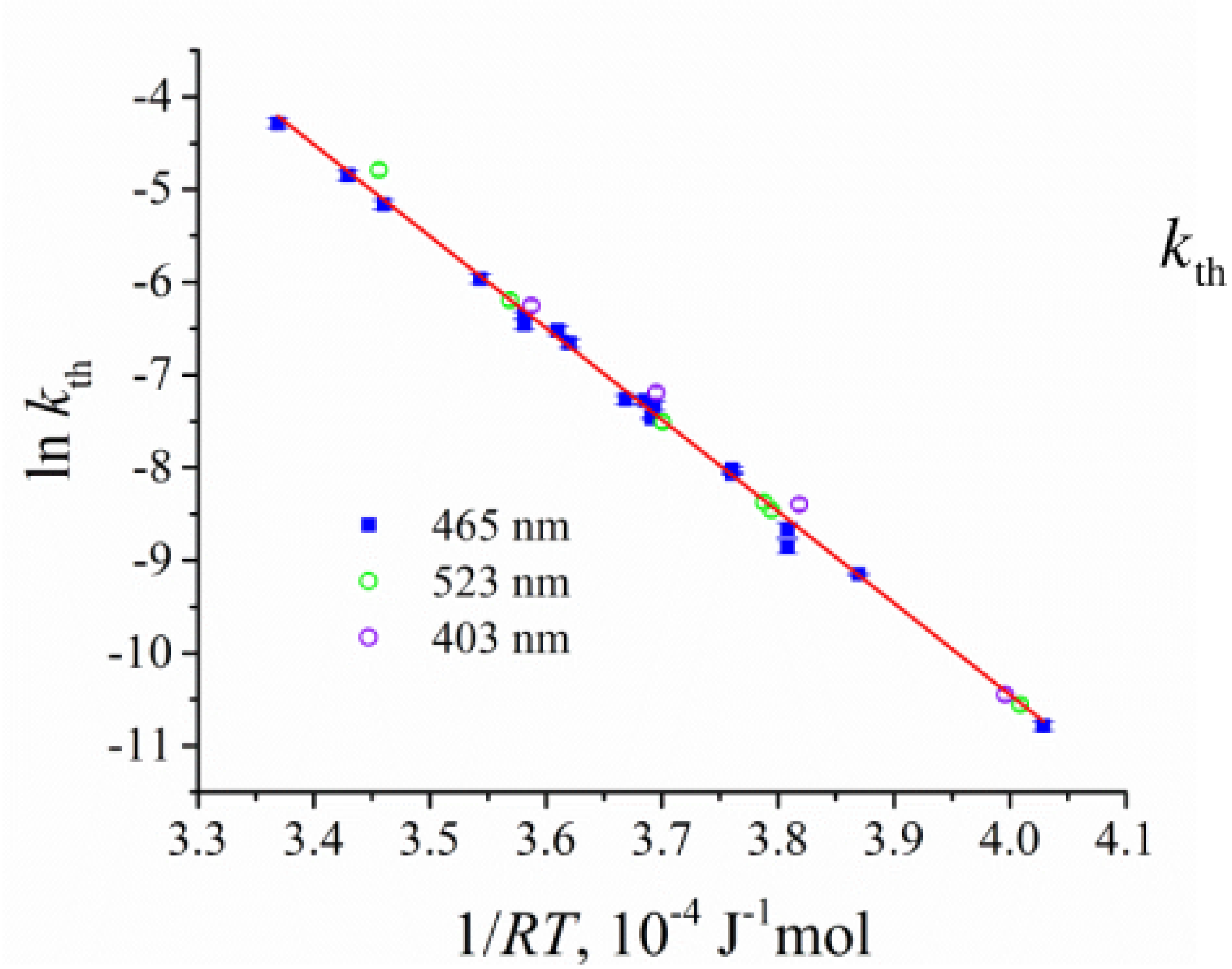
Independence of thermal isomerisation on previous photoisomeriation at different wavelengths



$$k_{\text{th}} = 3\times10^{12}\,s^{-1}\exp\left(-\frac{98\,\text{kJ/mol}}{RT}\right)$$

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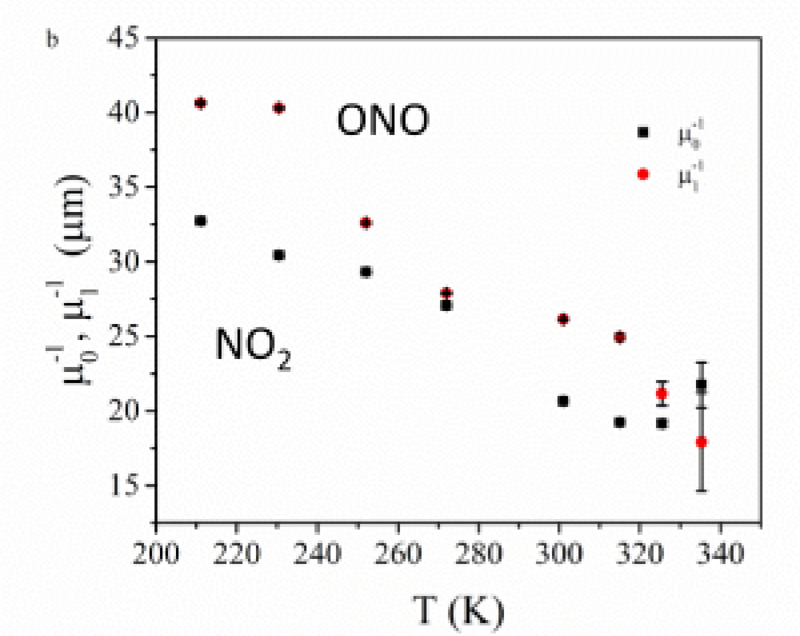
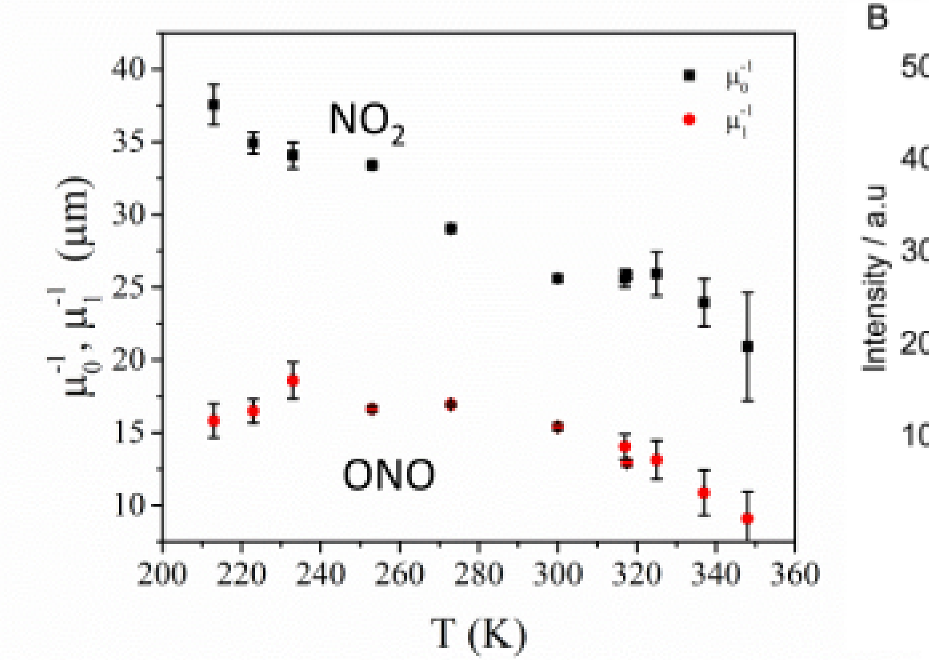
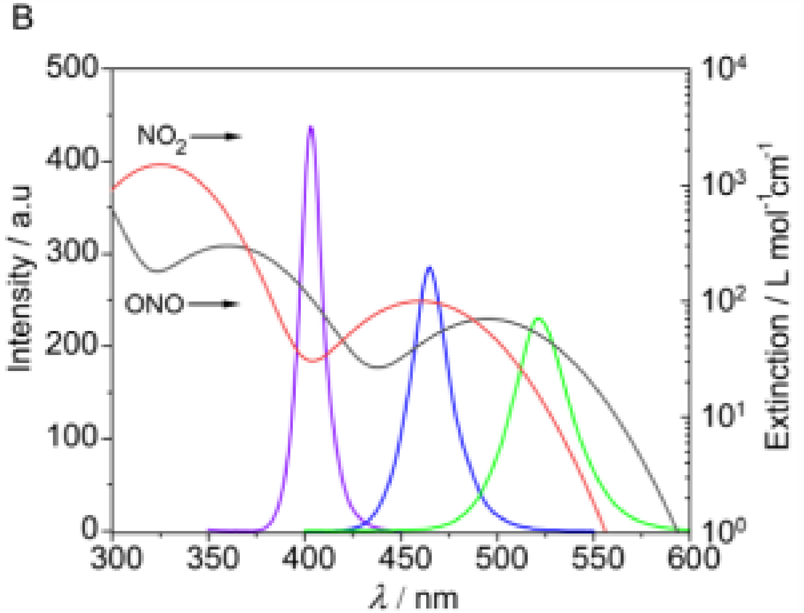
Absorption coefficients

Violet
403 nm



Green
523 nm



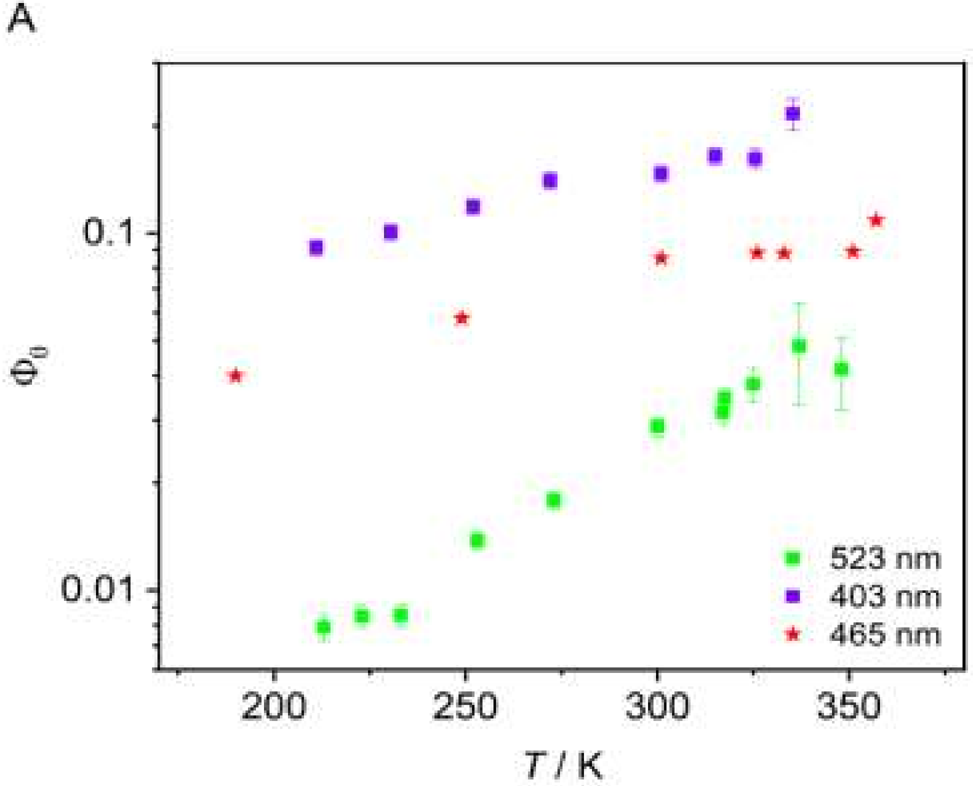


Blue, λ=465 nm:

NO$_2$ μ_0^{-1}=(9±0.5) μm

ONO μ_1^{-1}=(34±1) μm

Quantum yield



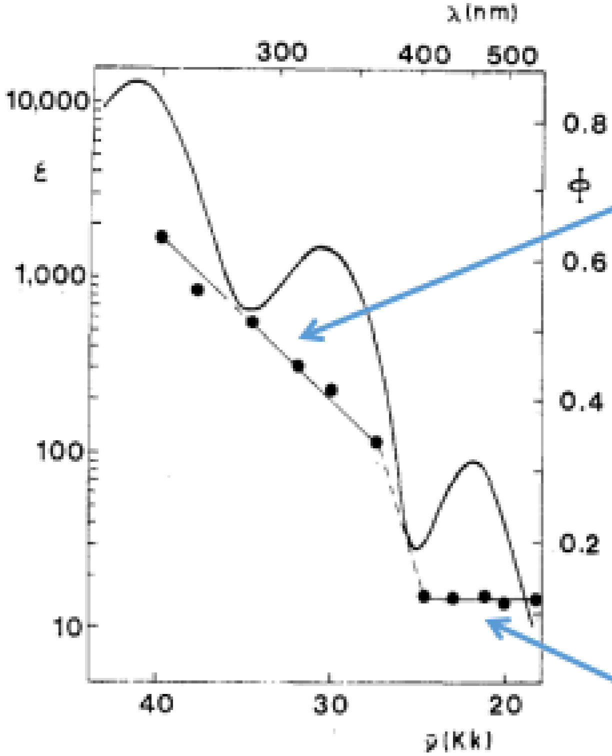
Quantum yield is rising with excitation energy and temperature

Higher excited states (charge transfer) increase probability of the isomerisation

Thermal expansion increases probability of the isomerisation

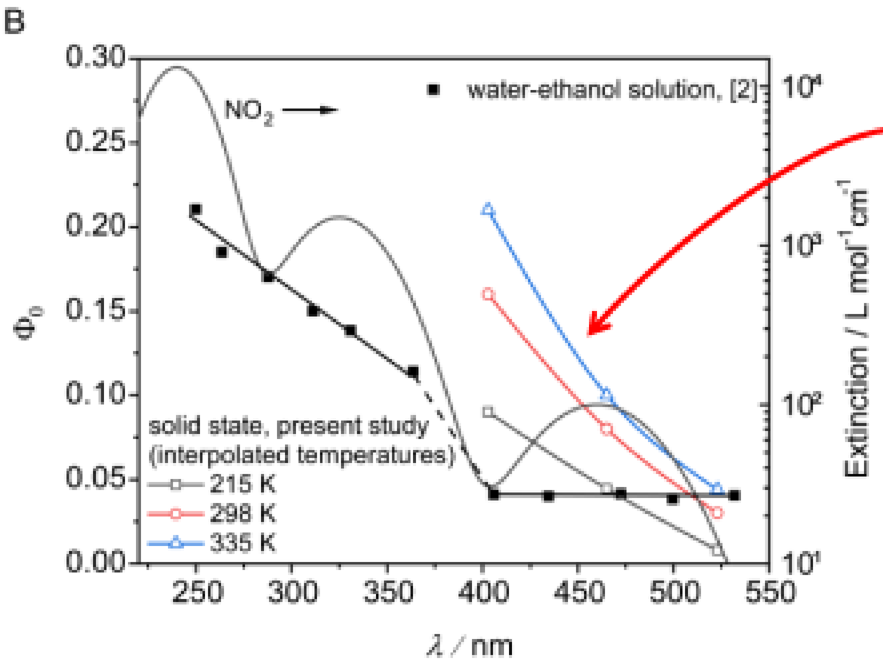
Wavelength dependence of quantum yield – solution vs crystal

Water-ethanol solution
F. Scandola, C. Bartocci and M. A. Scandola,
The Journal of Physical Chemistry, 1974, **78**



Quantum yield depends on excitation energy: isomerization is faster than the thermal equilibration of the excited state within CT bands

Quantum yield is constant: isomerization goes after thermal equilibration within d-d band



isomerization is faster than the thermal equilibration of the excited state in crystal even within d-d band

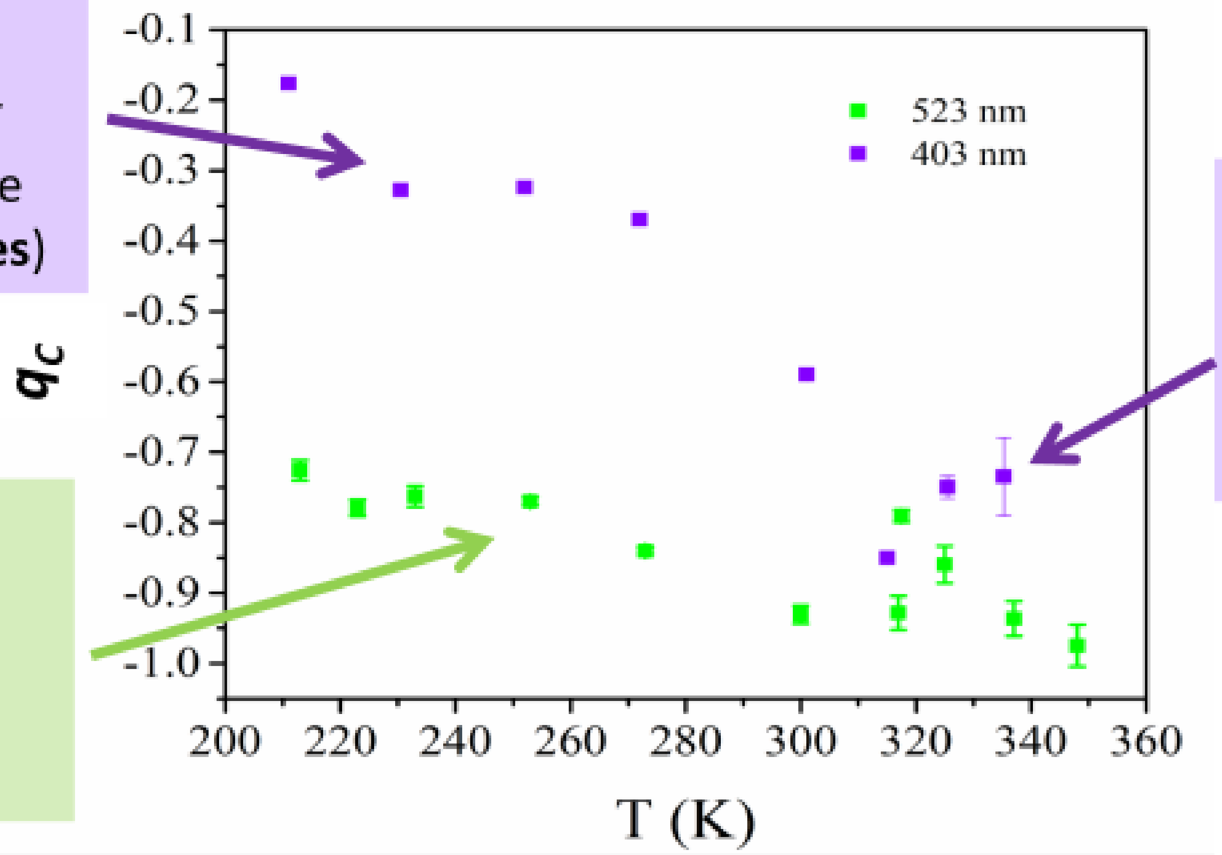
Dependence of the feedback effect on T and λ unveils contribution of different reactive excited states

$$\Phi\left(C\right)=\Phi_0\left(\lambda,T\right)\exp\left(q_C C\right)$$

λ=465 nm: q_C=-0.8 =>

Quantum yield decreases almost twice when transformation approaches 100% ONO. Qualitatively similar to the effect of external force and thermal expansion

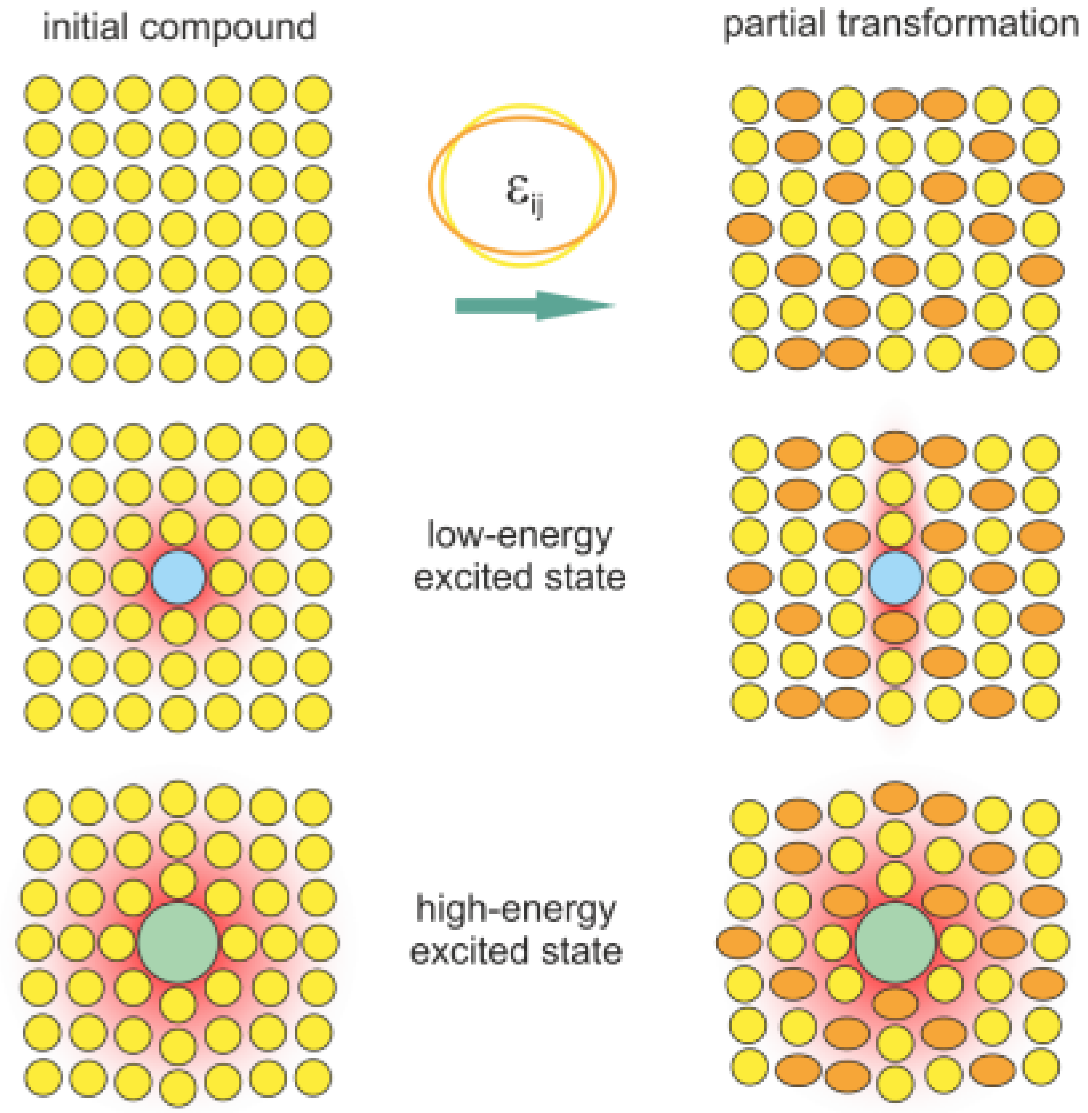
Lower feedback effect.
Lower sensitivity of reactive states to lattice strain (significant contribution of CT transitions at low temperature leading to **larger excited states**)



Increase of the feedback effect at higher temperature caused by increase of contribution by d-d transition

Higher feedback effect.
Higher sensitivity of reactive states to lattice strain (**smaller excited states** caused by d-d transition)

Dependence of the feedback effect on T and λ unveils contribution of different reactive excited states



Transformation causes lattice strain

Local lattice distortion by the smaller low-energy excited state is affected by the transformation lattice strain

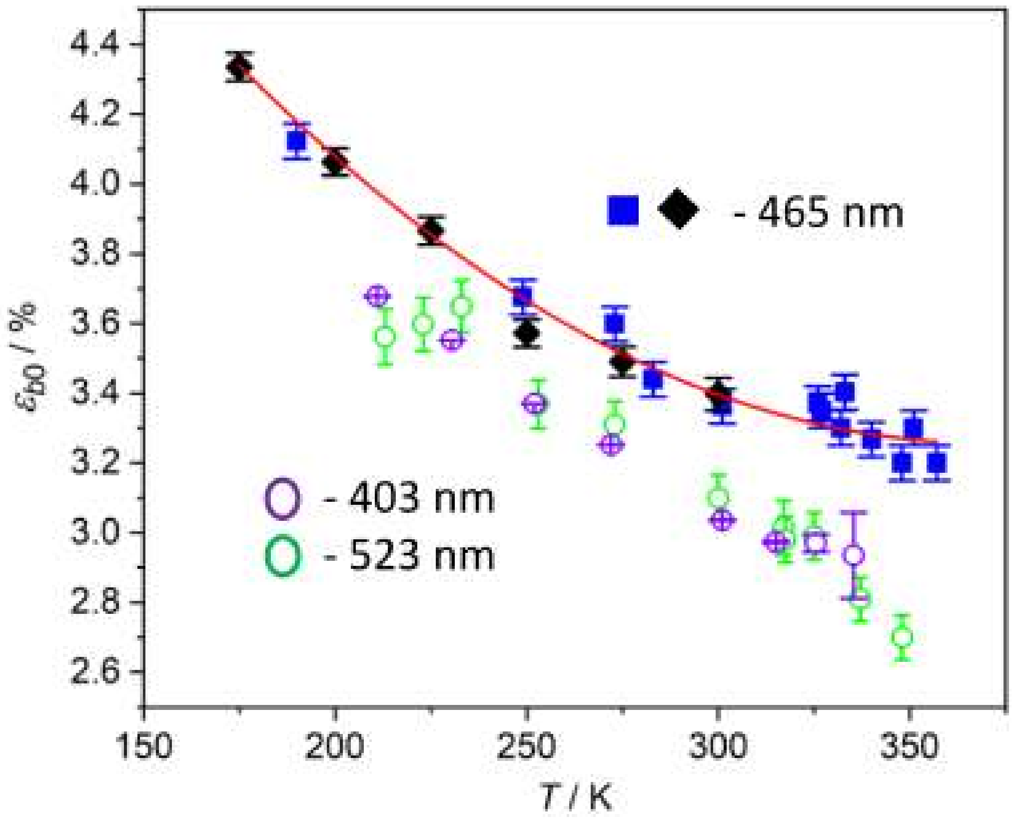
Larger sized high-energy excited state is less affected by the transformation lattice strain

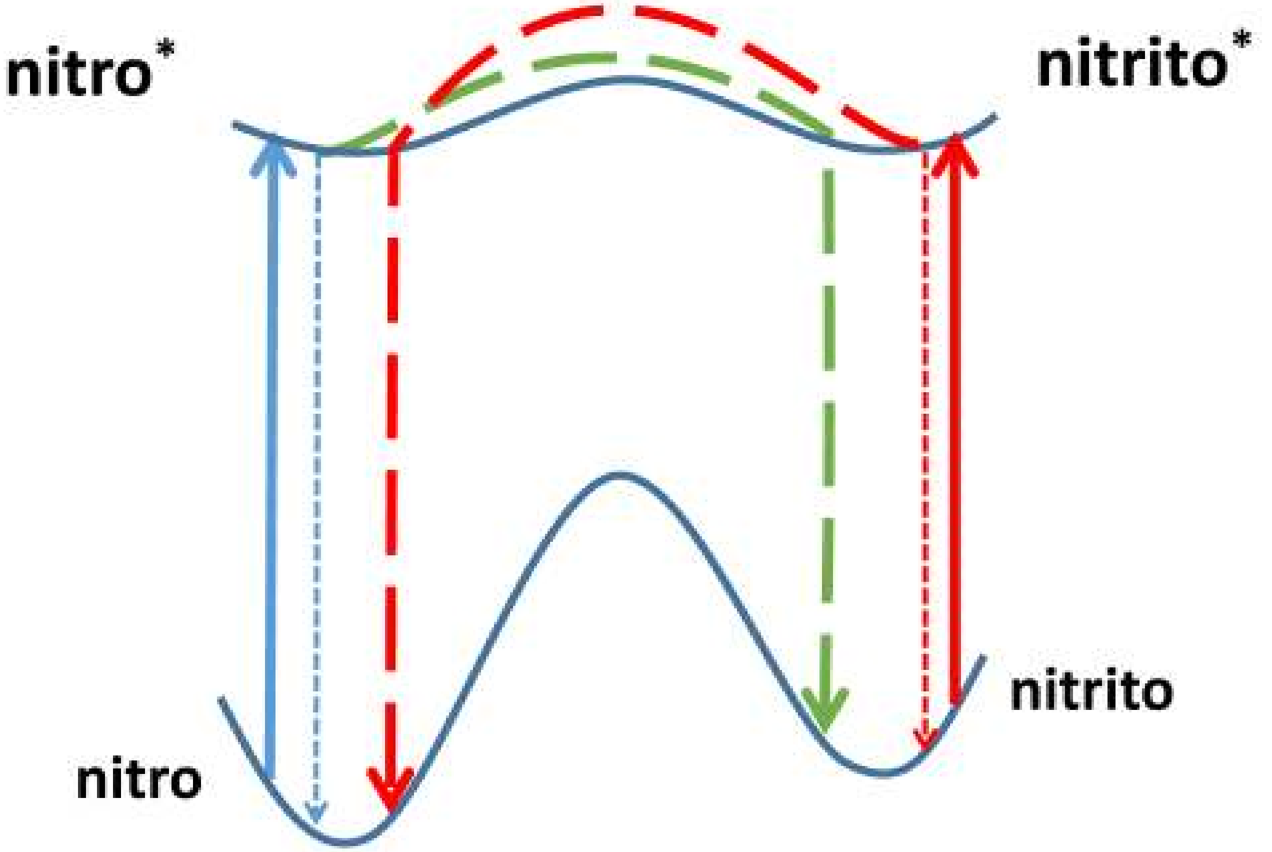
Maximum crystal elongation depends on wavelength

The maximum degree of isomerisation under green and violet is 10% lower than for the blue light source.

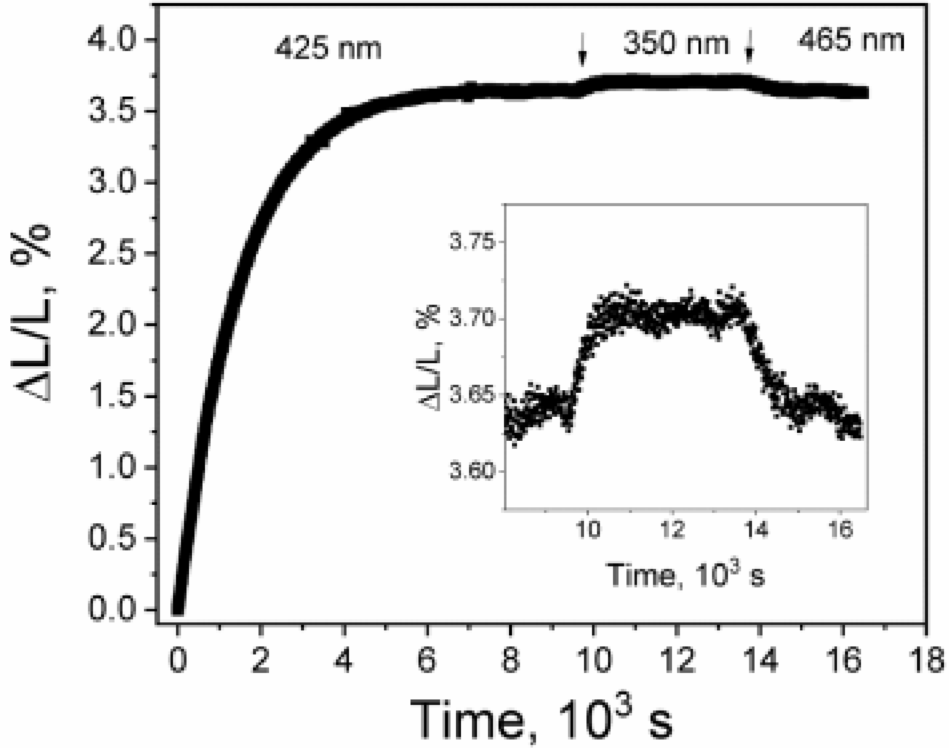
=>

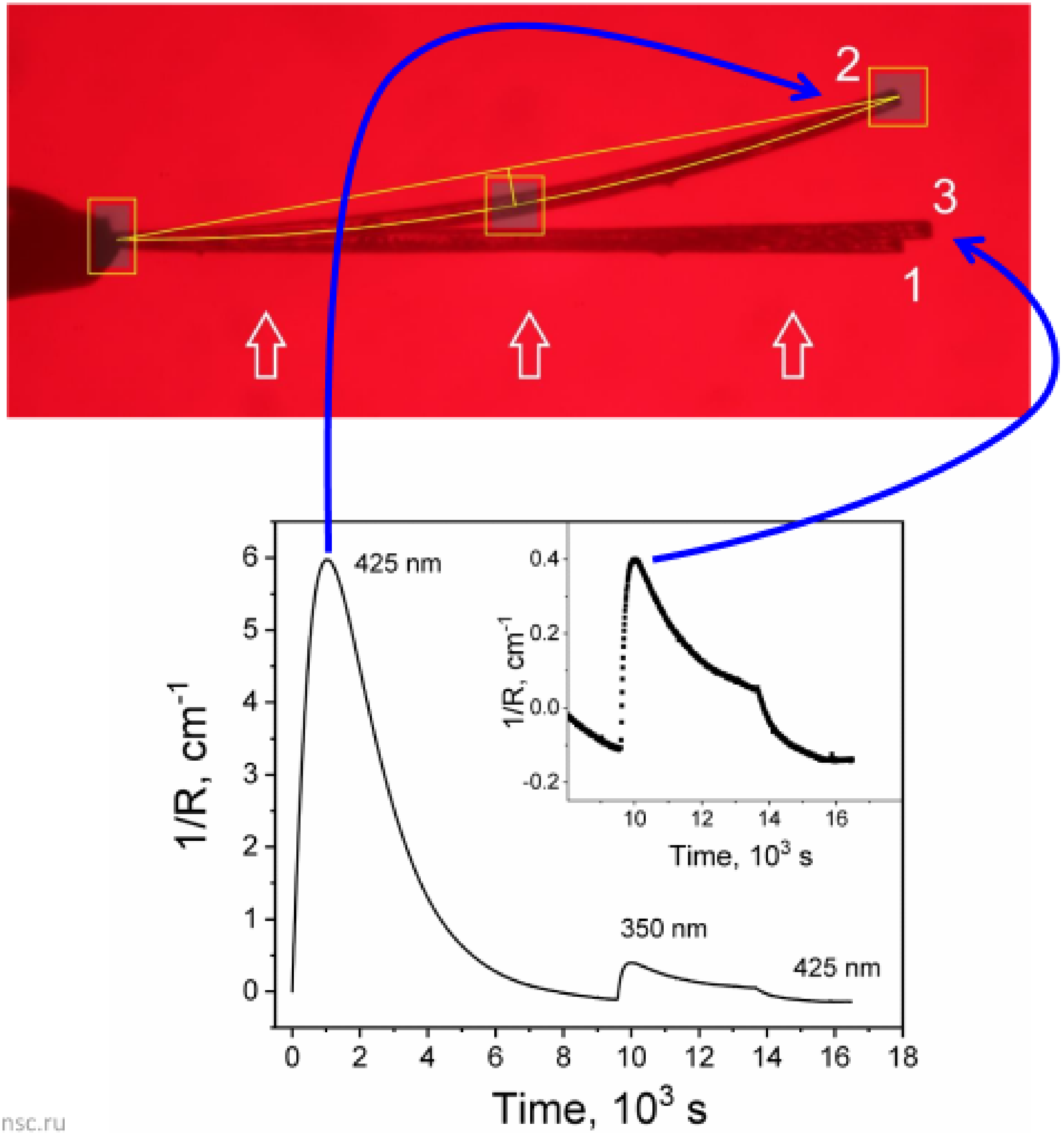
A sign of the reverse photoisomerization of nitrito to nitro





Crystal response to the wavelength change 425 nm – 350 nm – 425 nm





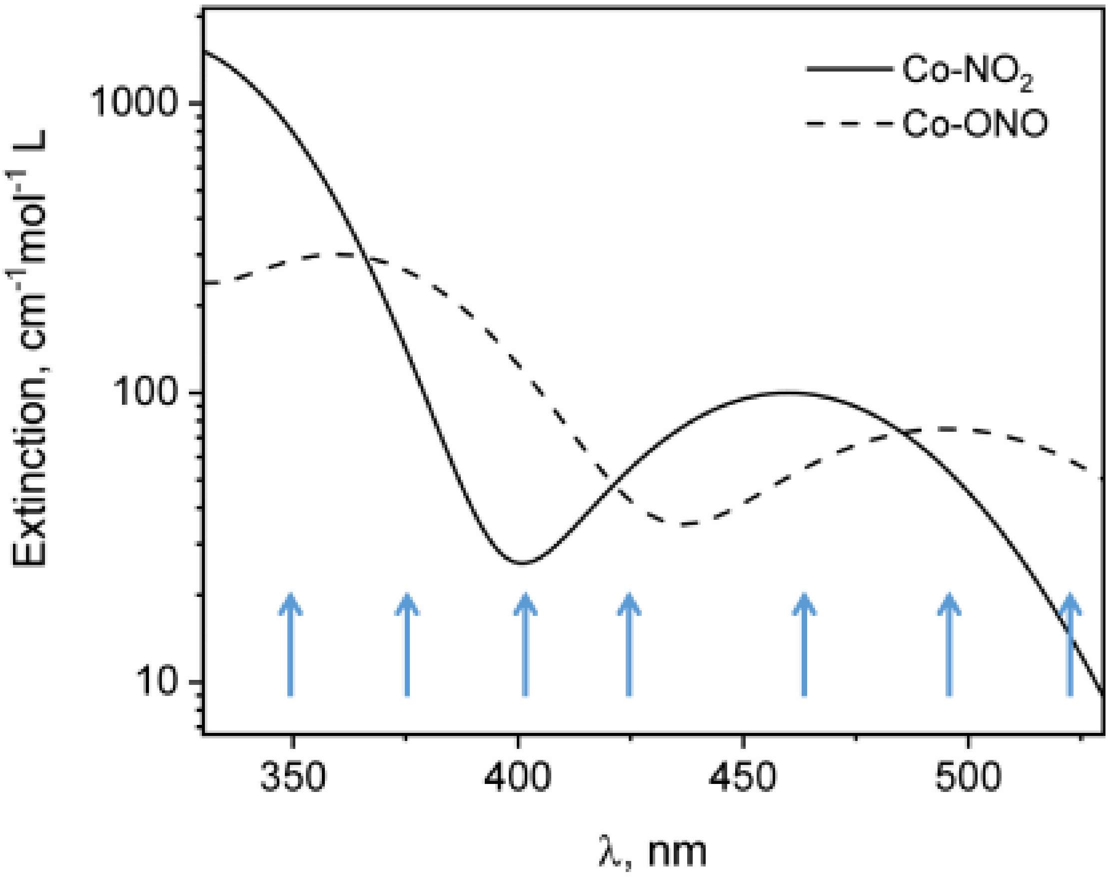
There is an additional reversible change in the crystal length by 0.08%. Difference in transformation degree ~ 2.2%

Additional objectives of the study

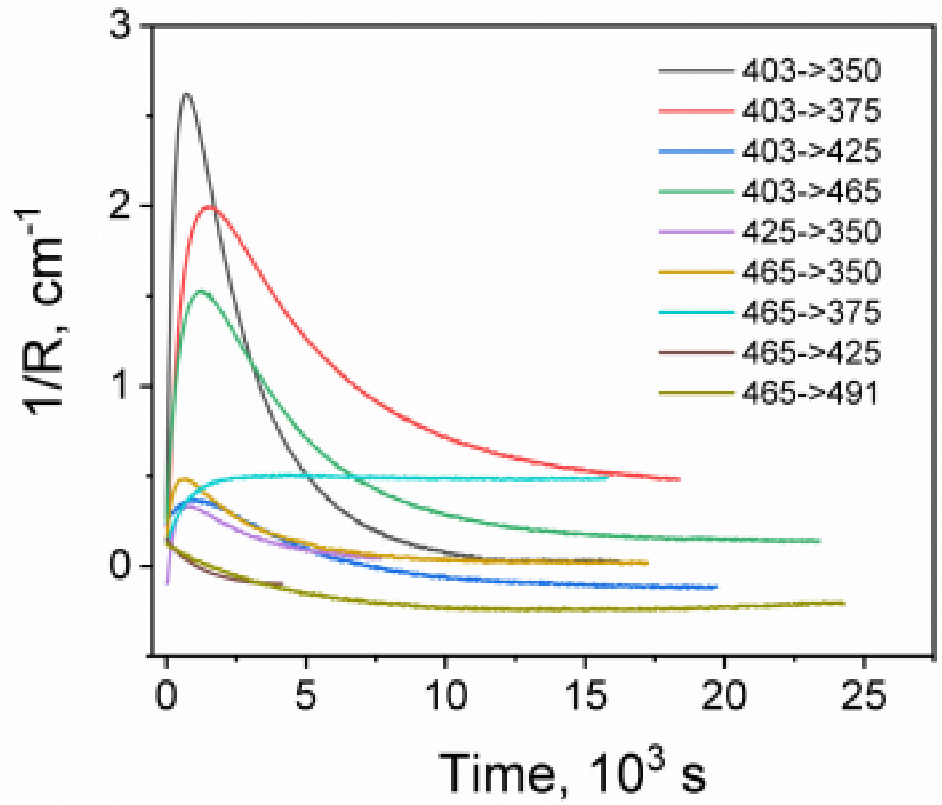
Study wavelength dependence of the photostationary isomerisation degree in $[Co(NH_3)_5NO_2]ClNO_3$ crystal by switching light sources at low temperature (0 °C):

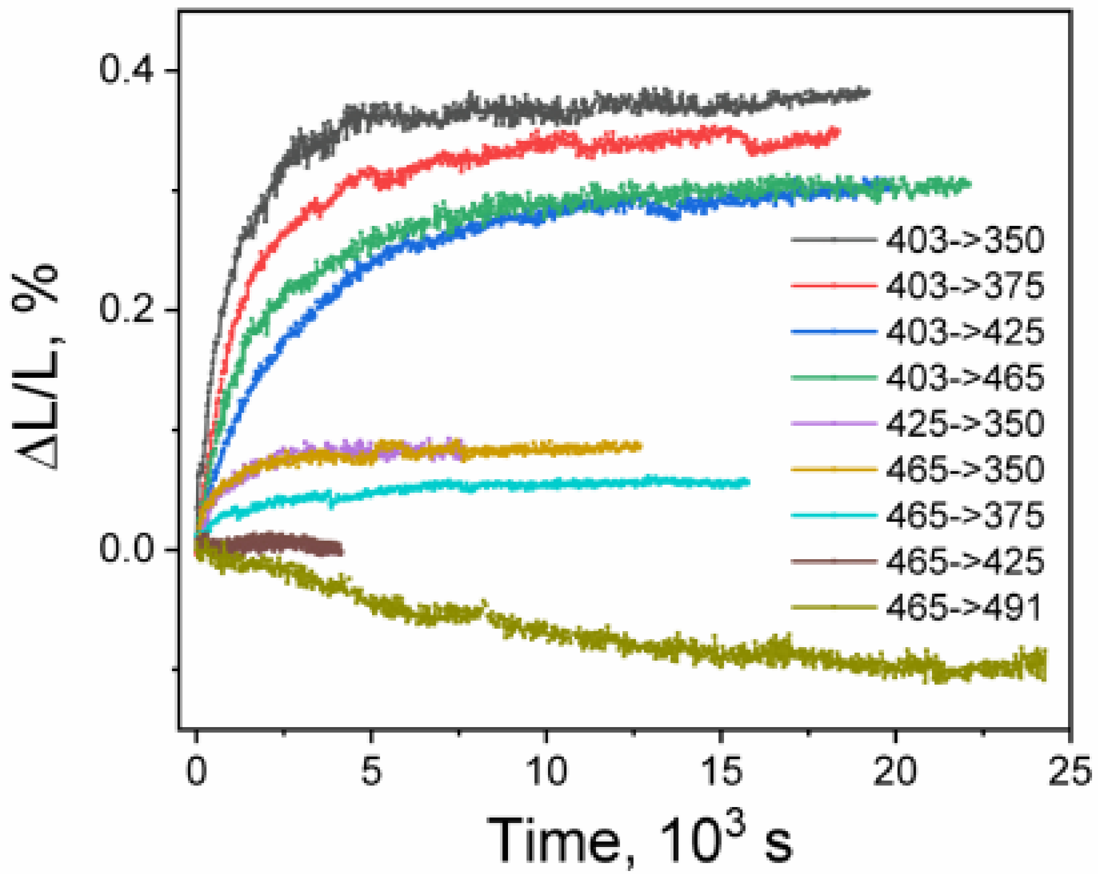
a. crystal is exposed to a selected light source till steady state
b. light source is changed; response is registered and analysed

wavelengths: 350, 375, 403,425, 465,491,523 nm



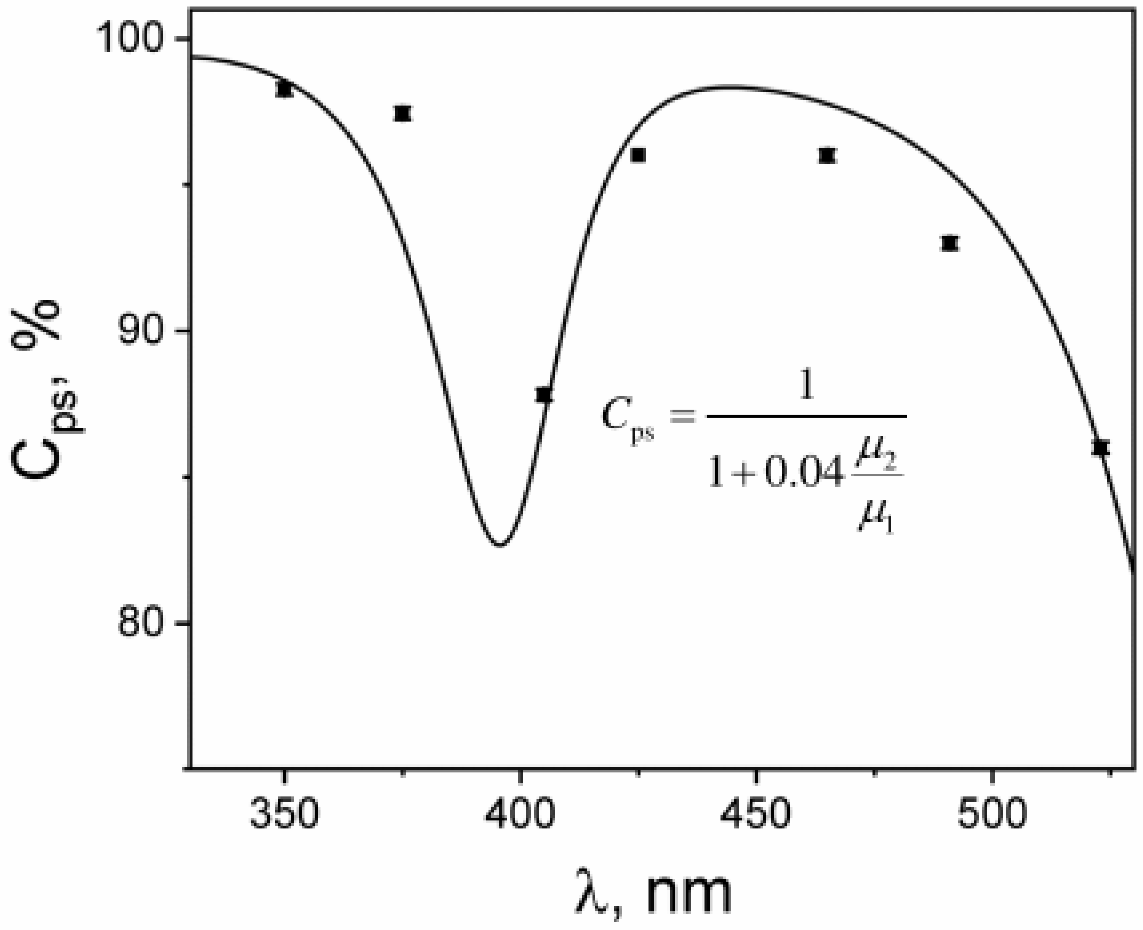
Crystal response on the wavelength change





λ, nm	350	375	403	425	465	491	*523
C_{ps} – C_{ps}(425 nm)	2.2%	1.5%	-8.2%	0	0	-3%	-10%
C_{ps}	98.3%	97.5%	87.8	96%	96%	93%	86%

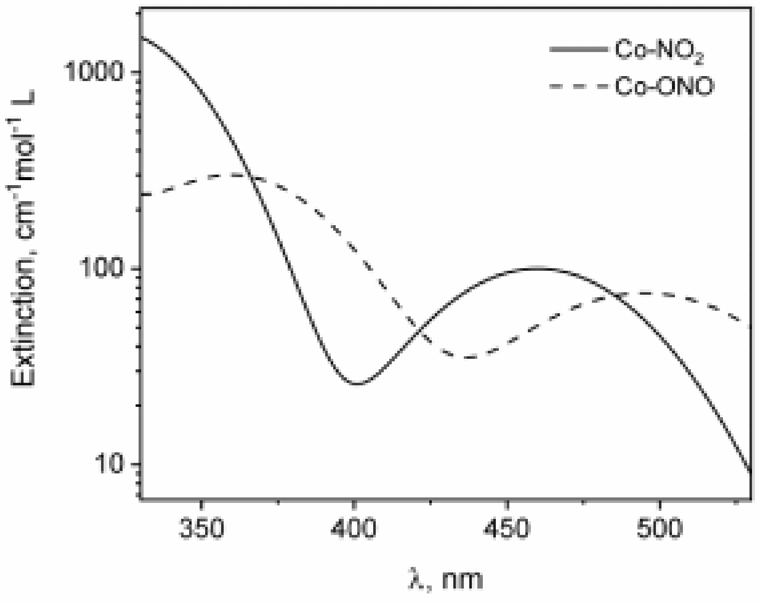
Wavelength dependence of the photostationary isomerisation at T=0 °C



$$\frac{\partial C}{\partial t} = k_1(1-C) - k_2 C = 0$$

$$k_i = I(x)\Phi_i \mu_i / C_0$$

$$C_{ps} = \frac{1}{1+\frac{\Phi_2 \mu_2}{\Phi_1 \mu_1}}$$



Photostationary transformation degree can be qualitatively explained if quantum yield of reverse isomerisation is ~0.04 of that for the usual nitro-nitrito isomerisation

$$\frac{\Phi_2}{\Phi_1} = 0.04$$

Conclusion made from the photomechanical response of $[Co(NH_3)_5NO_2]Cl(NO_3)$ crystals

- Absorption of light at 465 nm and 523 nm leads to the formation of identical reaction states with a high feedback coefficient q_C=-0.8. Excited states correspond to d-d transition in [Co(NH3)5NO2]2+ (460 nm band)
- Radiation at 403 nm leads to the formation of reaction states that are less sensitive to lattice strain q_C=-0.2, which indicates a significant fraction of transitions in the charge transfer band (325 nm)
- Evidence of reverse photoisomerisation of ONO to NO_2 was found
- Wavelength dependence of the photostationary degree of isomerisation has been determined for λ=350-523 nm. The stationary fraction of ONO lies in the range of 88-99% with a local minimum at λ=403 nm, corresponding to the minimum absorption by NO_2
- Quantum yield of the reverse nitrito-nitro photoisomerisation is estimated as 0.04 of the forward reaction