

# Photothermal study of structural relaxation in supercooled glycerol by fast fluorescence thermometry

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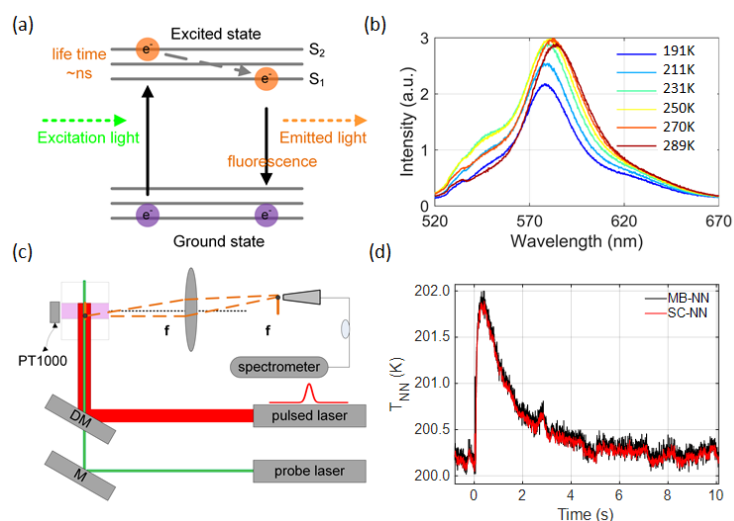
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**Background** – Structural relaxation refers to a part of the response to a stimulus (e.g. mechanical) of glassforming liquids being slow, due to the involvement of time-consuming cooperative changes of the atomic or molecular network, with a characteristic relaxation time that strongly increases with decreasing temperature [1]. In case the stimulus is (photo)thermal, the response to the optically supplied thermal energy can be observed both as a volume change (thermal expansion) and a temperature change. The temperature change gives information on how the supplied thermal energy is distributed over different vibrational degrees of freedom. Given sufficient time, in a relaxing material, part of the thermal energy is channeled from vibrational energy to configurational energy. Many methods have been proposed to observe this “thermal relaxation”, which is typically quantified by invoking an effective frequency- dependent heat capacity  $C(\omega)$ : the 3- $\omega$  technique [2], photopyroelectric spectroscopy (PPE) [3,4], and AC-chip nano-calorimetry [5]. The volume response to supplied heat can be expressed by a frequency- dependent thermal expansion coefficient  $\gamma(\omega)$ , which can e.g., be characterized using capacitive scanning dilatometry [6]. The above methods have limited bandwidth. In the following, we report on an all-optical photothermal approach to characterize the frequency dependence of the heat capacity of glycerol. The detection of fast temperature changes is achieved by fluorescence-based thermometry [7].

**Methods** – Fluorescence-based thermometry is based on the temperature dependence of the fluorescence spectrum (in this work: Rhodamine B (RhB)). The concept is depicted in Figure 1(a). Optically excited electrons go back to the ground state, releasing their stored energy by emitting a photon, i.e., fluorescence light. The energy and thus wavelength of the emitted photons is determined by the previous interactions of the electron with vibrational motions in the surroundings. The temperature dependence of these interactions makes the fluorescence spectrum temperature-dependent. The fluorescence lifetime of RhB is of the order of nanoseconds, making it feasible to use the evolution of the spectrum as a fast, optical quantifier of temperature. Figure 1(b) shows the temperature-dependent fluorescence of RhB in glycerol. The peak wavelength, full-width-at-half-maximum (FWHM), and the integrated intensity of the fluorescence are all sensitive to the temperature variations, and these relations can be calibrated and parametrized by model functions or trained neural networks (NN) [7].

In order to characterize thermal relaxation in glycerol (purity>99%), the sample was doped with RhB with a low concentration,  $2 \times 10^{-6}$  mol/L, making it fluorescent. Copper chloride (CuCl<sub>2</sub>) was added (0.1 mol/L) to enhance the absorption of the sample to the pump laser (1064 nm, 50 mJ/pulse, 8 ns pulse duration, Quantaray®). As shown in Figure 1(c), the fluorescence emission of RhB was excited by a CW-532 nm probe laser (06-DPL, Cobolt®) and was continuously collected by a fiber-coupled

spectrometer. During the experiments, the starting temperature of the sample (before the photothermal excitation laser pulse) was measured by a platinum thermometer near the region of interest.



**Fig. 1.** (a) Fundamentals of laser-induced fluorescence: Jablonski energy diagram of the excited molecule; (b) Fluorescence emission spectra of RhB at different temperatures; (c) Experimental setup for fluorescence-based thermometry implemented in a pulsed photothermal measurement; (d) Reconstructed photothermally induced temperature evolution by two different spectral shape based neural networks (“multi-band” and “spectral-shape”) after stimulating the sample with a single laser pulse.

**Results** – Figure 1(b) shows the temperature dependence of the fluorescent intensity spectrum. Both the intensity and shape (redshift) change with temperature. By making use of calibration curves or a trained neural network, these spectra were used to extract the temperature from the fluorescence spectrum both during static and dynamic heating) experiments. Figure 1(d) shows an example of an experimental trace of the measured temperature response when the sample was subjected to transient photothermal heating from the ns laser pulse. The extraction of the temperature from the normalized (to the maximum value) fluorescence spectrum was done by two different neural network configurations that used 4 bands of the spectrum (multi-band - MB) and the detailed spectrum (shape-based - SC), respectively. The main challenge of this approach is to combine a high signal-to-noise ratio (SNR) on the collected fluorescence signals with a high acquisition speed. Without averaging, the noise limit of the implemented experimental setup was around  $20 \text{ mK/Hz}^{1/2}$ .

## References

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