Fluorescent molecular rotor probes nanosecond viscosity changes

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ABSTRACT

Viscosity is a key property of liquids, but it is difficult to measure in short-lived, metastable samples due to the long measuring times required by conventional rheology. Here, we show how this problem can be solved by using fluorescent molecular rotors. The excited-state fluorescence decay rate of these molecules is sensitive to the viscosity of their local environment, and by combining pulsed laser excitation with time-resolved fluorescence detection, we can measure viscosities with a time resolution of a few ns. We demonstrate this by measuring in real time the viscosity change in glycerol induced by a nanosecond temperature jump. This new approach makes it possible to measure the viscosity of extremely short-lived states of matter.

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properties of 4-DASPI have been very well characterized, in particular the relationship between its fluorescence decay and the viscosity.\textsuperscript{6-9,14,30,31} We study solutions of 4-DASPI in glycerol with a concentration of \( \simeq 40 \) \( \mu \)M, which is sufficient to detect the fluorescence, while excluding potential inner filter effects and possible interactions between fluorophores while in the excited state. In fact, at the concentrations used in our experiments, the average distance between the 4-DASPI molecules is about 20 nm, \(^7\) which is several orders of magnitude larger than the average displacement by diffusion while in the excited state (\( \simeq 1 \) ns).

A simplified sketch of the experimental setup is shown in Fig. 1(a). The sample is kept in a quartz cell with a thickness of 1 mm. A near-infrared (NIR) pulse (8 mJ/pulse) with a duration of \( \simeq 4 \) ns [Fig. 1(b)], a bandwidth of 2 nm, and a focal beam diameter of 700 \( \mu \)m is used to generate the temperature jump. Its wavelength is resonant with the overtone of the OH-stretching mode of glycerol [Fig. 1(d)], and since the excited vibrational modes relax to the ground state within a few ps, the temperature increases nearly instantaneously. At the selected wavelength, roughly 70\% of the NIR pulse is absorbed, meaning that the heat is deposited throughout the optical path through the liquid and not only at its surface. The peak temperature (\( \Delta T \)) and pressure jump (\( \Delta p \)), achieved at the center of the pump beam, can be easily estimated, assuming a Gaussian profile for the NIR laser, using the relations\(^1\)

\[
\Delta T = \frac{E_p \alpha}{\pi D_0 p \rho C_v}, \quad \Delta p \approx \frac{\beta}{\kappa_f} \Delta T, \quad (1)
\]

where \( E_p \) is the energy of the T-jump pulse, \( \alpha \) is the absorption coefficient, \( D_0 \) is the beam diameter, \( \rho \) is the density, \( \beta \) is the coefficient of thermal expansion, and \( \kappa_f \) is the isothermal compressibility. Using Eq. (1) and assuming an initial temperature of 295 K, we estimate \( \Delta T \approx 8 \) K and \( \Delta p \approx 17 \text{ MPa} \) for our experiment. The NIR laser operates at a frequency of 20 Hz, and to avoid subsequent T-jump pulses hitting the same spot, the sample is scanned through the beam at an average velocity of 25 mm/s, which changes the illuminated spot every shot. During the experiments, the continuous exposure to the 20 Hz pulse train of T-jump pulses causes an overall temperature increase in the sample volume, which, in turn, causes convective heat transfer from the sample cell to its surroundings. As a consequence, during the experiment, the sample cell is at a temperature that is a few degrees above the ambient temperature (this steady-state temperature is reached within a few seconds after switching on the T-jump laser). To probe the viscosity, the fluorescence of 4-DASPI is excited in the center of the T-jump beam profile using a delayed counter-propagating ultra-fast visible pulse (\( \simeq 150 \) fs, 4 \( \mu \)J/pulse) with a smaller beam diameter (\( \simeq 220 \) \( \mu \)m) and a wavelength of 490 nm, close to the maximum of the excitation spectrum of 4-DASPI [Fig. S1(a)]. The absorption of 4-DASPI in our sample is \( \simeq 0.15 \) (Fig. S2), meaning that 75\% of the probe beam is transmitted: this ensures that the heated volume is homogeneously probed. The time-evolution of the fluorescence is detected at 90\° using a fast photodiode (Thorlabs, DET025A/M-2 GHz). To maximize the amount of detected fluorescence photons, we used only low-pass filters, cutting off all wavelengths below 565 nm: this ensures that most of the 4-DASPI fluorescence is detected, while the scattering

![Image](https://example.com/image.png)

**Fig. 1.** Setup for T-jump experiments with molecular rotors. (a) Schematic of the setup. A near-IR pulse (\( \simeq 4 \) ns) creates the T-jump, while the fluorescence of DASPI is excited by employing a counter-propagating visible pulsed beam (\( \simeq 150 \) fs). A fast photodiode is used to detect the emitted fluorescence in a 90\° geometry. (b) Time profile of the NIR laser pulse. (c) NIR absorption spectrum of glycerol (optical path length, 1 mm). The arrow indicates the frequency of the NIR temperature jump. This absorption band (1580 nm) is a combination of the overtone of the OH-stretching and bending mode of glycerol. (d) Green diamonds: fluorescence decay of 4-DASPI in glycerol at 295 K upon excitation by the visible laser pulse, as detected by the fast photodiode. The curve was obtained by averaging 1000 excitation shots. Black solid line: curve obtained by fitting the fluorescence decay with an exponential convoluted with the detector response (black dashed line).
from the probe beam is suppressed [see the emission spectrum in Fig. S1(b)]. We detect the fluorescence decay by directly recording the photodiode output with a 1 GHz digital oscilloscope (Keysight Technologies, DSA341A), which makes it possible to detect the complete fluorescence decay on a single-shot basis. Figure 1(d) shows an example of fluorescence decay as measured in glycerol at room temperature (green diamonds) along with the instrumental response function (black dashed line), the width of which is determined using the photodiode and oscilloscope response times. The fluorescence decay can be well fitted by a single exponential decay convoluted with the detector response (black solid line). The latter was measured by reflecting onto the detector a small fraction of the visible excitation pulse, which has a much shorter duration ($\simeq 10$ ps) than the photodiode and oscilloscope responses. 4-DASPI is characterized by a bi-exponential decay, but given the width of the instrumental response, these two components are not resolved, and we observe the mean value of the two decay constants. This observation is confirmed by the good agreement between the lifetime extracted by our fitting procedure ($\tau = 1.17(3)$ ns) and the amplitude-averaged lifetime (see also the discussion in Ref. 34), expected for the viscosity of glycerol (99%) at ambient conditions (see discussion in Sec. S2 of the supplementary material). This result also confirms that the visible laser pulses used to excite the fluorescence of 4-DASPI do not heat up the sample. Figure 2 shows the evolution of the lifetime in response to the T-jump: the increase in pressure increases the viscosity by maximum $\simeq 10\%$, resulting in a much smaller effect compared to the associated temperature jump ($\simeq 8$ K), which leads to a decrease in viscosity by $\simeq 50\%$ (see, for instance, Refs. 36 and 37 and references therein). It is also important to stress that the fluorescence of 4-DASPI is not directly sensitive to temperature in the range that is considered here but only to the viscoelastic properties of the sample. Figure 2(b) shows the lifetime at longer delay times. During this time window, the temperature of the sample remains essentially constant. After 0.5 ms, the sample start moving to a new position so that the next T-jump impinges on a fresh spot. The data of Fig. 2 can be directly converted into time-dependent viscosity using the quantitative relationship between the fluorescence lifetime $\tau_f$ and viscosity $\eta$ (the Förster–Hoffmann equation) as follows:

$$\tau_f = k \cdot \eta^x,$$

where $k$ is a constant and $x$ is the order of the relationship.
where $k$ and $x$ are parameters depending on the solvent and the fluorescent dye. These parameters can be determined independently from steady-state measurements on water–glycerol solutions with different viscosities (see Sec. S2 of the supplementary material), and using their values, we extract the time-dependent viscosity of glycerol in response to the T-jump. Molecular rotors are sensitive to the viscosity at the microscopic scale, which may differ from the macroscopic viscosity. However, in the case of glycerol at ambient conditions, we do not expect such heterogeneity (as is confirmed by the experimentally observed single-exponential fluorescence decay), and the macroscopic and microscopic viscosities are identical. The result is shown in Fig. 3(a). The isochoric heating of glycerol is accompanied by a sudden change in the viscosity, which, probed 10 ns after the T-jump, shows a decrease of $\approx 40\%$. As a consistency check, we used the known temperature dependence of the viscosity of glycerol$^{7,17}$ to estimate the magnitude of the T-jump from the observed viscosity jump (see the right y axis of Fig. 3). We find a value of $\approx 6$ K, in good agreement with our initial estimate of 8 K.

The results presented here show that fluorescent molecular rotors, combined with ultrafast optical excitation and fluorescence detection, make it possible to measure the viscosity of metastable states in liquids and to directly observe viscosity changes occurring at the ns scale. This unprecedented time-resolution opens up new possibilities to investigate the viscoelastic properties of short-lived systems, in particular of liquid states prepared using temperature jumps. An example is provided by the recent experiments of Kim et al.$^{11}$ who showed that T-jump experiments can provide access to the liquid–liquid transition of water. By ultrafast heating high-density amorphous ice into the no man’s land, they could observe a liquid–liquid transition in water taking place starting at $\approx 10$ ns after the T-jump, while crystallization occurred after a few $\mu$s. The liquid–liquid transition can be observed only because of the combined temperature ($\Delta T \approx 100$ K) and pressure jumps ($\Delta P \approx 2.5$ kbar), with the liquid–liquid coexistence line of water located at positive pressure. Our results indicate that molecular rotors can be used to measure the viscosities of these two short-lived liquid phases. In the high-viscosity regime, molecular rotors become progressively less sensitive to viscosity,$^{39}$ but we expect that in the experimental conditions of Ref. 1, it should be possible to measure the viscosity of supercooled water in no man’s land. In fact, in these experiments, high-density amorphous ice immediately devitrifies after the T-jump, and the resulting liquid state has a relatively high self-diffusion coefficient ($D_{H2O} = 2 \times 10^{-12}$ m$^2$/s). Hence, the conversion between the two liquid phases occurs in a regime of molecular mobility that is even higher than the one investigated here (for comparison, the self-diffusion coefficient of glycerol at ambient conditions is $D_{gly} = 1.37 \times 10^{-12}$ m$^2$/s).$^{40}$ Similarly, molecular rotors can also provide insights into the rheological properties of superheated liquids and solids generated using temperature jumps.$^{3}$ Furthermore, since molecular rotors are sensitive to viscosity at the microscopic scale, they can also reveal spatial heterogeneity in short-living states of matter: in the presence of a heterogeneous environment, the fluorescence decay will be characterized by a distribution of lifetimes.$^{41}$ Thus, the method presented here makes it possible to measure the viscosity in systems and states that are completely inaccessible to conventional rheology.

See the supplementary material for details on the spectral properties of 4-DASPI and the calibration of its lifetime dependence on viscosity.

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**AUTHOR DECLARATIONS**

**Conflict of Interest**

The authors have no conflicts to disclose.

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**Figure 3.** Viscosity of glycerol (green diamonds with error bars) as a function of the delay between the pump and the probe laser. (a) Close up of the time-zero region (10 ns–400 ns). The black solid line is obtained by fitting the data with a step function. (b) Semi-logarithmic plot of glycerol viscosity in the long-time region (10 ns–400 $\mu$s). The right y-axis reports the temperature of the sample during the T-jump, extracted from the temperature dependence of the viscosity of glycerol.


