



Triplet solvation dynamics in hydrogen bonding liquids in hard and soft confinements

Vincenzo Talluto¹, Carl Böhmer¹, Thomas Walther¹, Thomas Blochowicz²

¹Institute of Applied Physics, ²Institute of Condensed Matter Physics, TU Darmstadt (September 2013)

Introduction

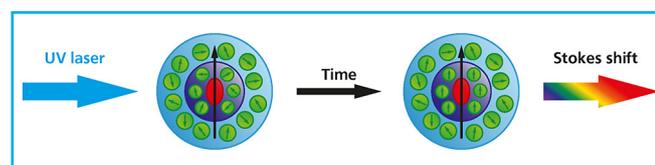
Many liquids show a dramatic change in their molecular dynamics when subject to a confining environment. The effects of the confinement on a liquid range from a suppression of crystallization below a certain pore size to an upshift or downshift of the glass transition of supercooled liquids within the pores. However, a separation of surface, density and finite-size effects in classic spectroscopic techniques, which average over the macroscopic sample, is very difficult. With the method of triplet solvation dynamics it is possible to locally access the relaxation dynamics.

Principle

As in dielectric spectroscopy (DS), triplet solvation dynamics (TSD) measures the reorientation of the molecular dipoles of a liquid as a response to an electric field. The difference lies in the generation of the electric field. Instead of applying a macroscopic electric field over the entire sample, the field is generated locally in the sample itself. This is done by adding a dye to the sample in a very low concentration. When pumping the dye with a pulsed UV Laser, it can be excited in a long-lived triplet state. Since the dipole moment of the triplet state differs from the ground state dipole moment, the surrounding liquid molecules start to reorient in response to the changed electric field of the dye molecule. Due to the relaxation of the surrounding liquid, a Stokes shift of the emission wavelength of the dye occurs, which can be measured in the time range from 1 millisecond to 1 second by time resolved optical spectroscopy [1]. From the measured Stokes shift positions $\langle\nu(t)\rangle$ one can compute the so called Stokes shift correlation function:

$$C(t) = \frac{\langle\nu(t)\rangle - \langle\nu(\infty)\rangle}{\langle\nu(0)\rangle - \langle\nu(\infty)\rangle}$$

$\langle\nu(0)\rangle$ and $\langle\nu(\infty)\rangle$ represent the emission frequency of the unshifted and the completely shifted system respectively. The spatial range of TSD is limited to the first solvation shell around the dye, making it possible to measure the relaxation dynamics locally in confinements of a few nanometres.



Schematic of Solvation Dynamics: dye molecule (red), solvation shell (dark blue), molecular dipoles (green).

Application Note

Experimental setup

The dye is excited in the triplet state by the third harmonic of a pulsed Nd:YAG laser (Innolas Spitlight 600) at 355 nm. To avoid bleaching of the dye the pulses are attenuated to a few mJ. The sample is mounted in a contact gas cryostat (Cryovac Conti Spectro 4), and can be temperature controlled in the range from 320 K to 77 K by a controller (Lakeshore Model 336). The emitted light is collected under 90° to the incident laser beam by a liquid light guide fibre. The output of the fibre is collimated into a grating spectrograph (Andor Shamrock SR-500i-A), which is equipped with a 150, 600 and 1800 lines/mm grating turret. An ICCD camera (Andor USB iStar DH340T-18F-03) is used to record the time-resolved emission wavelength of the dye. The setup is shown in fig. 1. During data acquisition the gate delay and

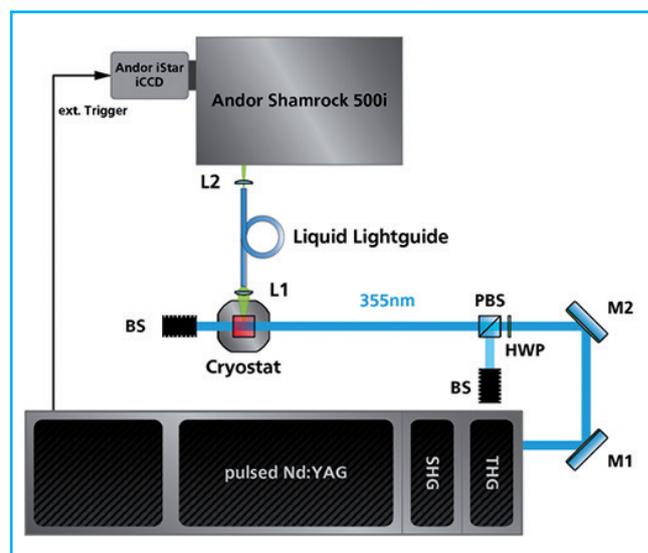


Figure 1: Schematic view of the TSD setup

width are controlled by an automated script written in "Andor Basic". Because of the fast shutter speeds that go down to 5 ns, it is possible to measure the solvation dynamics even in a short-lived singlet state. The short gate width of the camera will be especially helpful for the planned extension of the experimental setup, where the dye will be excited by two laser pulses in the UV (320 nm) and in the IR (940 nm) simultaneously. This will allow a much faster and more efficient population of the triplet state and therefore extend the useable time range down from 1 millisecond to 100 nanoseconds by using the STIRAP technique [2]. Fig. 2 shows the luminescence of the dye (Quinoxaline) inside the cryostat.

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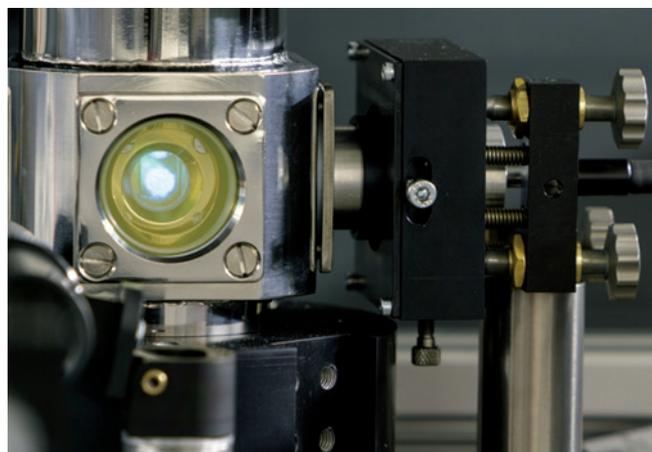


Figure 2: Dye luminescence and fibre optics

Application Note

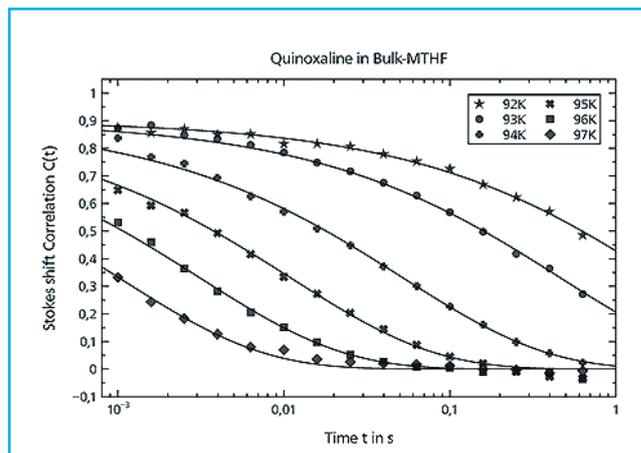


Figure 3: Stokes shift correlation function of Quinoxaline in MTHF

Results

After completing our setup we were able to make first measurements on simple glass-forming liquids. The first system we investigated was 2-Methyltetrahydrofuran (MTHF), a polar solvent suited for low temperatures down to 77 K. It has a glass transition at 91 K, with a very strong temperature dependency (fragile system). Fig. 3 shows the correlation function $C(t)$ at different temperatures. As can be seen, the whole dynamic process takes place within only 5 K. The data is fitted with a stretched exponential decay of the form:

$$f_{KWW}(t) = e^{-(t/\tau_{KWW})^{\beta_{KWW}}}$$

The stretching exponent of this Kohlrausch-Williams-Watts function β_{KWW} was fixed to 0.5 for all curves. The data is in very good agreement with the model. For this measurement the delay after the laser pulse was increased such that the spacing between the single data points is constant on a logarithmic time axis.

Furthermore we also investigated the mechanical relaxation of the non-polar solvent 3 Methylpentane (3MP). Here the delay was fixed at 15 milliseconds after the laser pulse and the temperature was varied instead. The recorded phosphorescence spectra are shown in fig. 4. These were recorded with the 150 lines/mm grating.

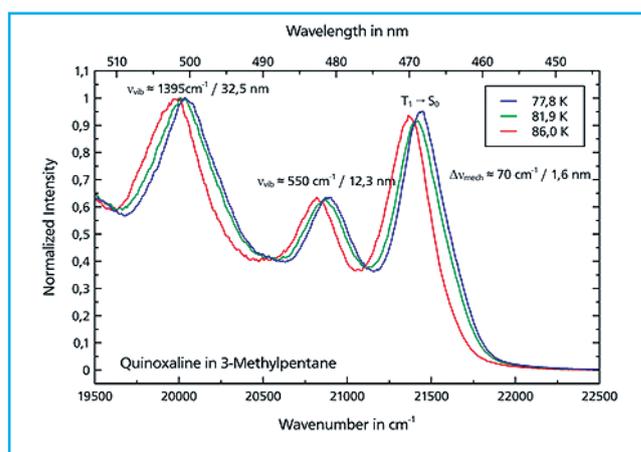


Figure 4: Stokes shift of Quinoxaline in 3MP.

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Application Note

Conclusion

We were able to set up a completely new triplet solvation dynamics experiment to investigate the influence of confinements on the molecular dynamics of glass-forming liquids. Being able to quickly select between coarse and fine gratings, makes it very easy to find the right settings for the measurements. The ICCD with its high sensitivity allows to measure in reasonable time, although the excitation of the dye and thus the generation of phosphorescence light is very inefficient with the current setup. At the same time the camera has a very high speed, which will be essential for the planned, more advanced setup.

References

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- [2] Bergmann, K., Theuer, H., & Shore, B. (1998). Coherent population transfer among quantum states of atoms and molecules. *Reviews of Modern Physics*, 70(3), 1003–1025. Retrieved from http://rmp.aps.org/abstract/RMP/v70/i3/p1003_1

Contact

M.Sc. Vincenzo Talluto
Technical University Darmstadt
Institute of Applied Physics
64289, Darmstadt, Germany

Email: vincenzo.talluto@physik.tu-darmstadt.de

Web: <http://www.iap.tu-darmstadt.de/lqo/>