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Liquid dynamics in ZrO_2 nanoporous films

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Abstract

Time-resolved Optical Kerr Effect (OKE) measurements were used to determine the orientational dynamics of water and acetonitrile in the bulk and in pores of ZrO_2 nanostructured films. The experiments were performed with a home-built OKE microscope, capable of providing the necessary axial resolution (5 μm) to exclusively probe the internal volume of the film. The time constants obtained for the orientational dynamics of the bulk liquids agree with the literature. In the pores, both liquids exhibit slower dynamics, indicating a restricted motion of the molecules at the interface. In the case of water, our data is manifestly incompatible with the existence of a bulk-like population of molecules in the core of the pores, suggesting that the interface induces a long range constraint on the orientational dynamics of the molecules within the nanocavity. The differences observed between the two liquids are interpreted as due to the H-bond character of water, which is absent in acetonitrile.

Keywords: Ultrafast dynamics; Interfaces; Water; Acetonitrile; Zirconium dioxide; Optical Kerr effect; Microscopy

1. Introduction

The dynamics of liquids at interfaces and in microconfinement, has attracted considerable attention in recent years, mainly due to their relevance for different fields including tribology, nano-machining, electrochemistry, chromatographic separation and biological hydration [1–5]. Many studies agree that liquids behave differently at an interface as compared to the bulk, but much remains to be learnt about this subject. Surface-specific techniques like time-resolved second harmonic and sum frequency generation, represent a valuable means to study the dynamics of liquids at interfaces [6,7]. However, these techniques cannot help understanding how the dynamic properties of the bulk are modified as one approaches the interface, because the signals intrinsically vanish in the centro-symmetric bulk systems. On the other hand, many experimental studies aim at a direct comparison between the dynamics of liquids in the bulk and at interfaces. Two main approaches are commonly applied. In the first one, a dye molecule attached to the surface is used to perform an ultrafast solvation study, either by fluorescence up-conversion [3,8,9], super-continuum transient absorption [5], or photon echo [4,5] techniques. The same experiment performed with the dye in bulk solvent, provides a reference to reveal the specific dynamics at the interface. A general drawback of this approach consists in the impossibility of probing the two environments under identical conditions. Indeed, the modification of the dye properties at the interface, and the direct contribution of the solid to the solvation process, makes the interpretation of the results not straightforward [5,10]. In the second type of approach, a molecular probe is not used, and the dynamics are probed in a non-invasive way by non-linear optical methods. Optical Kerr Effect (OKE) spectroscopy, is a particularly well-suited technique for elucidating the dynamics of liquids, for it provides a direct measurement of the orientational time correlation function of the liquid [11]. In order to probe the interfacial behavior using this technique, the liquids can be studied confined in nanoporous media, which provide a large and controllable

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surface-to-volume ratio. OKE studies performed on this kind of systems, have already proven to be a powerful tool for determining the dynamic and even structural properties of liquids at interfaces [1,12–15]. However, these studies have been restricted so far to liquids embedded in a reduced number of silica sol–gel glasses. The application to other nanoporous media is severely constrained by the necessity of transparent, high optical quality materials.

The production of good optical quality nanoporous films of other materials, like TiO_2 and ZrO_2, has been intensively studied thanks in great part to the interest they present for applications in photoelectrochemical solar cells [16,17]. Performing OKE spectroscopy on liquids confined in these media, would provide valuable insight into the properties of these interfaces, actively used in many industrial applications, including paints and cosmetics, bio-compatible materials, self-cleaning windows, anti-fog coatings, and photoelectrochemical cells. The main obstacle to perform this kind of studies, is the relatively small thickness of the films that can be prepared with a reasonable optical quality (less than 10 μm). A high spatial resolution is required to allow a distinct OKE measurement of the liquid confined in the film, from the bulk liquid that surrounds it. A similar problem was confronted by Potma et al., when measuring the OKE signal of intracellular water, to compare its dynamics with that of bulk water [2]. To this purpose, they developed an OKE microscope which allowed to obtain a signal from a volume of a few cubic microns; small enough to discern the intracellular space of a living kidney cell from the surrounding aqueous medium. The same principle has been applied here to study the dynamics of two liquids (acetonitrile and water) in the inner region of an 8 μm-thick ZrO_2 nanoporous film. The two liquids investigated here are strongly polar, and wetting at the ZrO_2 interface. Nevertheless, we can expect some differences in their behaviors, because acetonitrile is an aprotic solvent, while water is a strongly H-bonded, self-associative liquid.

In Section 2 of this paper, we provide a detailed description of the OKE microscope and the preparation of the sample cells. The first part of Section 3 is devoted to the characterization of the performance of the microscope, particularly concerning its axial spatial resolution. Next, we present and discuss the results obtained for the reorientational dynamics of water and acetonitrile in bulk and in the films. These results are correlated with recently published literature on similar studies.

2. Experimental section

2.1. Sample preparation

The ZrO_2 films were prepared according to the procedure described by Grätzel and co-workers in several publications [17,18]. The sol paste was kindly provided by J-E. Moser and P. Comte from the Laboratory of Photonic and Interfaces of the Swiss Federal Institute of Technology, Lausanne. The paste featured particles of roughly spherical shape with an average diameter of 12.4 nm. From N_2 adsorption and desorption measurements (Brunauer Emmett Teller, BET), the porosity of the sol–gel was estimated to 57%. The average pore size was 11 nm.

The films were prepared on glass microscope cover slips ($24 \times 50 \times 0.15$ mm, Menzel-Glaser). Following the published recipe [18], stripes of the sol paste were deposited on the glass by doctor blading, dried in air for a few minutes, and then heated for 10–12 min at 450 °C with a hot air blower (Leister Hotwind-S 9C1 3700 W) to eliminate the binding polymer. The films obtained by this preparation presented 7–8 μm thickness, as calibrated in a profile-meter (Alpha-Step 200, Tencor Instruments).

The freshly prepared films were assembled in closed cells as illustrated in Fig. 1. Both windows and spacers were made of thin microscope cover slips (Menzel-Glaser, $24 \times 50 \times 0.15$ mm), to obtain a total cell thickness of approximately 0.5 mm, thus allowing to place the sample between the microscope objectives in the setup.

To avoid evaporation of the solvents, the cells were sealed with wax. Holding together the windows and spacers, the long flanks of the cell and the bottom edge were sequentially immersed in wax at 65 °C. At room temperature this liquid solidifies within seconds, sealing the cell on these three sides and keeping the parts together. Normally three to four immersions were repeated in sequence to guarantee a hermetic sealing. The cell was then filled through the open edge and rapidly closed with wax. The whole process of assembling, starting from the removal of the ZrO_2 film out of the hot air flow, until the final cell was sealed on every side, was generally performed in no more than 2 min. All measurements were performed on freshly prepared cells. No signs of sample degradation or

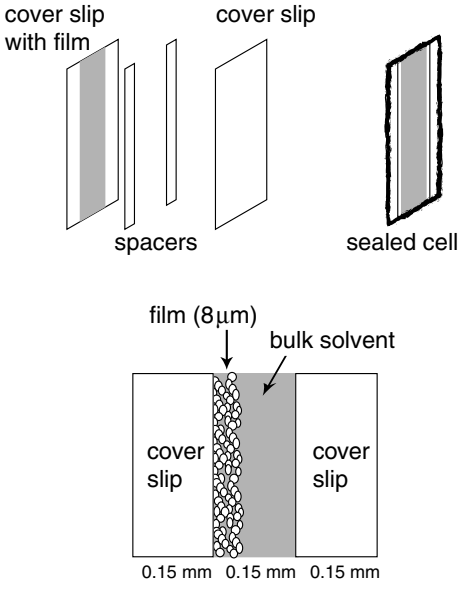

Fig. 1. Assembling of the cell for OKE microscopy. The lower scheme represents a profile of the cell as viewed from the side (not scaled).