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Single Molecule Spectroscopy: Translational and Rotational Diffusion of Single Fluorescent Dyes in Nano-Structured Porous Materials

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1. Introduction

Single molecule spectroscopy (SMS) is a powerful tool to characterise interactions between a molecule and its immediate environment, revealing details of these interactions and their variability from molecule to molecule. The translational and rotational diffusion of single molecules inside various mesoporous solids can be investigated with this method. It provides insight into the channel or cage structures of the hosts and their influence on the behaviour of the guest-molecules inside.

2. Observation of individual diffusing molecules

Fluorescent dye molecules (Terrylenediimide TDI, Streptocyanine 9A1) were incorporated into the pores of various mesoporous materials (SBA, MCM type materials, Sol-Gel-Glasses) in very low concentration, so that they could be observed individually via fluorescence microscopy. Two SMS techniques were applied: wide-field imaging and confocal microscopy, each having its own advantages.

2.1 Wide-field imaging: Translational Diffusion with high temporal resolution

Using wide-field microscopy sequences of images with a temporal resolution of down to 14 ms per frame were acquired. The positions of the individual fluorescing molecules could be tracked with a spatial resolution down to 20 nm (fig 1a). The resulting trajectories were analysed to characterise the translational diffusion of the molecules in different matrices. In all cases several sub-populations of differently diffusing molecules, including immobile ones, could be distinguished.

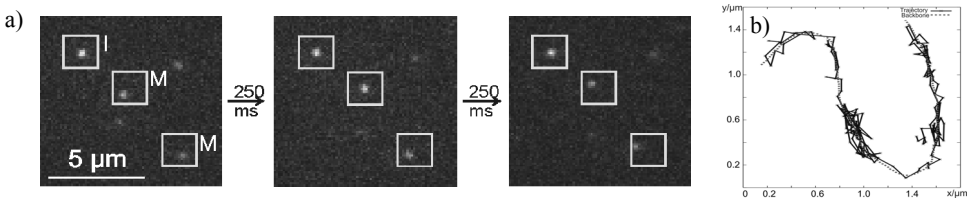

Fig. 1: a) Sequence of images acquired with the wide-field imaging setup (14 ms per frame; 17 frames (ca. 250 ms) are skipped between the depicted images). The fluorescence patterns of 1 immobile (I) and 2 mobile (M) molecules are highlighted. b) Structured trajectories occur in the case of a well-ordered system of channels like hexagonal SBA-15.

In the case of diffusion in relatively disordered Sol-Gel-Glasses a stronger deviation from isotropic Brownian motion occured in samples with an average pore diameter of 3 nm in comparison to samples with 22 nm sized pores. Molecules changing between immobile and mobile state within one trajectory could be observed.

In the more ordered hexagonal network of SBA-15 material in some cases the shape of the trajectories seems to reflect pore structure and topology of the host system (see fig. 1b). Additionally, less structured trajectories of faster moving molecules were detected.

2.2 Confocal microscopy: Simultaneous measurements of Translation and Rotation

The rotational diffusion of TDI in hexagonal pores with smaller diameter (MCM-41, pore diameter ca. 4 nm) is investigated simultaneously with their translational diffusion. Using polarisation-dependent confocal microscopy the in-plane angle can be obtained with a precision of a few degrees (fig. 2) and with a temporal resolution of 18s per frame. The diffusion coefficients in these samples are three orders of magnitude smaller than in the samples described above.

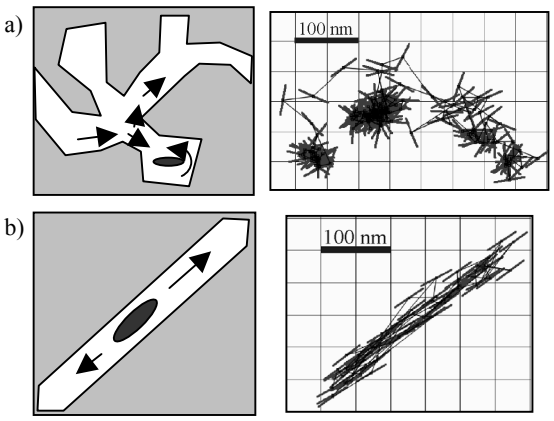

Fig. 2: Simultaneous measurement of translational and orientational diffusion.

a) Diffusion between different interconnected domains.

b) Movement along parallel pores: The orientation of the molecule is aligned parallel to the direction of the trajectory.

3. Conclusion

We demonstrated that SMS is a valuable tool for the detailed characterisation of molecular diffusion in porous systems. For the first time translational movements of a single molecule tumbling through a porous system could be directly correlated with its rotational motion.

References

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