

# INFLUENCING SINGLE MOLECULES ROTATIONAL MOTION BY LIGHT

Gabriel Dutier, V. De Beauhoudrey, Joseph Zyss, Sophie Brasselet\*  
Laboratoire de Photonique Quantique et Moléculaire (CNRS UMR 8537)  
Ecole Normale Supérieure de Cachan, Institut d'Alembert (IFR 121)  
ENS Cachan, 61 av. du Président Wilson, 94 235 Cachan, France  
\* present address : Institut Fresnel – MOSAIC, Marseille France  
E-mail : [sophie.brasselet@fresnel.fr](mailto:sophie.brasselet@fresnel.fr)

Antoni Mitus

Wroclaw University of Technology Institute of Physics, Wybrzeze Wyspianskiego  
2750-370 Wroclaw, Poland

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The rotational dynamics of single molecules in polymer matrices is currently studied with tools of increasing sophistication, using highly sensitive polarized confocal microscopy. Such a technique has recently allowed to elucidate the complex heterogeneous behavior of non-Gaussian statistics [1], providing new scales of investigation of local viscosity that would be otherwise not detectable in ensemble measurements.

In this work, we attempt to influence single molecules rotational behavior in a controllable way using optical polarized excitation, taking advantage of molecular mechanical deformations upon trans-cis photoisomerization [2]. Re-orientation of photo-isomerizable molecules under a resonant linearly polarized optical excitation originates from the angular randomization that follows excited-*trans* to *cis* state relaxation. After many cycles a global rotation perpendicular to the excitation polarization is expected to occur, stabilized by matrix re-organization. The complex dynamic process that leads to the final molecular orientational distribution is however not completely elucidated, and relies on phenomenological pictures of the re-orientation probability accounting for photo-isomerization quantum yield as well as the polarization and intensity of the excitation [2,3].

The experiments were performed on the DCM laser dye, which exhibits a reasonable compromise between fluorescence and photo-isomerization quantum yields [4]. Single molecules were dissolved in PMA or PMMA polymers matrices (T<sub>g</sub> 25°C and 120°C) and excited by a CW 473 nm laser source intermittent between a “re-orientation” time of linear polarization and a “read-out” time of circular polarization, allowing the real-time anisotropy measurement of the in-plane molecular orientation. Re-orientation has been observed [5], with a low efficiency and a stability improved in the high T<sub>g</sub> polymer environment. This low efficiency is understood by statistical analysis, which show large static heterogeneities and large fluctuations especially at low T<sub>g</sub>, indicating that re-orientation is mainly driven by thermal diffusion in both polymers. This is confirmed by a simple kinetic model applied to re-orientation, which accounts for both photo-isomerization and thermal diffusion probabilities and their T<sub>g</sub> –dependence [3]. This study evidences that the knowledge of polymer dynamics and the control of local environment are the main parameters to optimize in order to fully control molecular re-orientation towards the realization of molecular tweezers or molecular optical-gates.

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