TERS microscopy as a probe for visualizing the orientation of chromophores embedded in the glassy polymers

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Abstract. Photo-induced effects on azobenzene-functionalized polymer thin films under exposure to strongly focused higher laser modes are investigated. Tip-enhanced Raman scattering microscopy provides a possibility for probing and visualizing the orientation of anisotropic chromophores embedded in the glassy environment at room temperature.

1. Introduction
Azobenzene containing polymer thin films are technologically important structures. The appropriate electron-donor and electron-acceptor substitutes result in large polarizability and intrinsic dipole moment of azochromophores [1]. The ordering of dipoles produces a high optical nonlinearity and therefore the second harmonic generation (SHG) is observed in these patterns [2,3]. This is one of the research directions of azobenzene-based matter [4,5].

On the other hand thin films with azochromophores possess photomechanical properties [6,7]. This allows the creation of different structures on the film surface by the laser irradiation. For instance interesting application is the photo-assisted fabrication of the surface relief gratings [8,9]. Such structures can be used as diffractive optical elements [6]. Moreover, the periodical orientation of dipoles in such gratings is one of the approaches of increasing the SHG efficiency.

In our work we concentrate on the molecular motion induced by strongly focused laser beam with linear and radial polarization. The observed structures are analyzed with the use of tip enhanced Raman scattering (TERS) to estimate the presence of optical anisotropy.

2. Experiment and discussion
The movement of azopolymer is strongly dependent on the orientation of the incident light. We first consider the interaction of azopolymer with the linear polarized laser beam. It is assumed that the incident light is tightly focused by using the high aperture objective. The incident light firstly leads to the orientation of induced dipole moments (figure 1). Secondly the inhomogeneous optical field results in the arising of the gradient force [6]:

$$f = \frac{1}{4} \varepsilon_0 \chi' \exp(-\alpha z) \frac{\delta I(x,y)}{\delta x} \hat{x}_0,$$

where $\varepsilon_0$ is a permittivity of vacuum, $\chi'$ is the real part of the polymer medium susceptibility, $\alpha$ is the absorption coefficient of light, $I(x,y)$ is the intensity distribution of the Gaussian beam at the focal plane and $\hat{x}_0$ is the unit vector along the $x$ axis direction. Thus, the azobenzene chromophores experience the force only in the polarization direction along the component of the optical-field gradient, and the force is vanishing when the polarization is orthogonal to the optical field. The
moving of the polymer mass occurs only in the polarization direction and leads to the appearing of the transverse profile on the film surface.

![Figure 1](image1.png)  
**Figure 1.** The orientation and displacement of the dipoles in the Gaussian beam (top view).

We have confirmed this experimentally. The object of our investigation is 4-amino-4’-nitroazobenzene covalently connected to the main chain of the polymer matrix (CFAO) (fig. 2a) [10]. Amino group is the donor of electrons and nitro group is the electrons acceptor. CFAO was strongly diluted in cyclohexanone. The films were casted on slide cover glass at 5000 to 12000 rpm. Thereafter the films were annealed during 1 hour at a temperature of 100°C for removing solvent remains. A film thickness was estimated to be ~70 nm.

![Figure 2](image2.png)  
**Figure 2.** The structure of CFAO (a) and its absorption spectrum (b).

In order to produce the photoinduced surface deformation the polymer films with azobenzene were irradiated by the linearly polarized laser beam with the 633.8 nm wavelength which is far from the maximum of the absorption (fig. 2b). The exposure time was 100 s and the intensity at the center of a laser spot was about a few kW/cm². A high numerical aperture (NA=1.4) oil-immersion lens (100×) squeezes a laser beam into sizes less than diffraction-limited laser spot thus providing information on high spatial frequencies.

The linearly polarized light engraves a dip and pitch on the CFAO surface film at the centre and rims of the laser spot respectively. The topography and the cross section of the structure are shown in figure 3. A depth of the dip is approximately 3 nm and the diameter is about 1.5 µm. Maximal surface deformation was observed along the laser polarization. Thus, the experimental data are in agreement with the theoretical model.

![Figure 3](image3.png)  
**Figure 3.** AFM of polymer surface after linear polarized laser radiation (a) and its cross section along polarization direction (b).
Importantly, the deformation profile is primarily dependent on the light polarization. In particular, the radial polarization of the highly focused light beam permits the longitudinal field to be as great as the transverse field. For this purpose we implemented a four sectional radial polarizer consisting of four oriented half-waveplates (fig. 4).

Figure 4. Tightly focused radial polarized laser beam, longitudinal component enhanced by optical antenna (a) and optical field distribution (b). \( \rho = \sqrt{x^2 + y^2} \).

The use of the optical antenna results in the field enhancement by several orders of magnitude. The tip squeezes the far field over the extent of several nanometers and, thus, sub-wavelength patterns occur. In figure 5 the AFM image of the film surface after illumination by optical longitudinal field is shown. The protrusion with a height of 10 nm and a diameter of 100 nm appears at the centre of the laser spot.

Figure 5. AFM of polymer surface exposed to a tip-enhanced radial polarized light (a) and its cross section (b). The area of the laser beam placing is marked by dotted circle.

To analyze the molecular orientation we have compared Raman spectra of the CFAO film before and after corona discharge poling using the 632.8 nm excitation. We have found no difference between them at moderate intensities of the laser light. At higher intensities we have observed degradation and photobleaching of the CFAO film. This is evidenced by the irreversible appearance of a peak at 1130 cm\(^{-1}\), as shown in figure 6.

Figure 6. Raman spectra of the CFAO films with different exposure times. Figure 7. Near- and far-field Raman spectra of the CFAO film with the 632.8 nm excitation.
The absorption of chromophores depends on the polarization of incident light. Figure 7 shows a Raman spectrum of the original 70 nm thick film, that has been recorded with 632.8 nm radially polarized light for 100 s. TERS method allows one to probe the longitudinal anisotropy with a sub-wavelength spatial resolution, whereas the transverse anisotropy can be visualized with the diffraction-limited resolution.

The optical antenna can convert the far field into localized modes due to the plasmonic effect [11]. A hot spot beneath the tip apex is excited with longitudinal fields, which are parallel to the long axis of the conical antenna. Tip-enhanced Raman scattering comes from chromophores whose main polarizability components ($\alpha_{xx}$ or $\alpha_{zz}$) are oriented towards the longitudinal field. If one of the directions coincides with that of a dipole moment then we observe a giant absorption and photodegradation appears. The enhancement of a peak at 1110 cm$^{-1}$ provides evidence that chromophores are mainly aligned along the film surface rather than inward the bulk. As the chromophore gets oriented along the longitudinal field, it is inevitably photobleached and destroyed. Figure 8 demonstrates TERS maps of the oriented thin film at 1130 cm$^{-1}$ and 1400 cm$^{-1}$. The presence of the peak at 1130 cm$^{-1}$ (fig. 8a) is a result of chromophore orientation along the longitudinal field and, therefore, the molecule has been photobleached. On the other hand, 1400 cm$^{-1}$ peak (fig. 8b) indicates that the N=N bond for of out-of-plane anchored chromophores is conserved.

Figure 8. The Raman mapping of the CFAO thin films at 1130 cm$^{-1}$ (a) and 1400 cm$^{-1}$ (b) The area of the laser beam placing is marked by dotted circles.

3. Conclusion
The light-driven surface deformations of azobenzene chromophore containing polymer thin films were achieved by using linear and radial polarized incident light. It has been obtained TERS spectra of the thin films and found the feature for aligning chromophores in the thin film.

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