Polarized 3D Raman and nanoscale near-field optical microscopy of optically inscribed surface relief gratings: chromophore orientation in azo-doped polymer films

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Supplementary Information

Theoretical model

In our case we consider the uniaxial distribution of a population of chromophores with cylindrical symmetry.[46] Because of the cylindrical symmetry, the molecular polarizability tensor is given as[46]:

$$\alpha = \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_3 \end{pmatrix} \qquad (1)$$

The general expression for the collected intensity in Raman scattering for a given vibrational band is[46,48]:

$$I_{Raman} \approx KI_0 \sum_{ij} \left| \left(\alpha_{ij} \right) \right|^2 \qquad (2)$$

where K is a constant which depends on the density of the scattering centers, I_0 is the intensity per unit surface and α_{ij}, the derivatives of the molecular polarizability tensor element.
The measurements are recorded in the direct laboratory system (X, Y, Z), in the following we will use the reference axes of the molecular system (x, y, z). The transformation between the coordinate systems is obtained with the help of three Euler angles (θ, φ, ψ), using the general relation:

$$\left[\alpha_{XYZ} \right] = \left[T^t \alpha_{xyz} T \right] \qquad (3)$$

where T is a rotation matrix and T^t the transposed matrix. For any isotropic or anistropic medium averaged orientational quantities have to be considered[46]:

$$I_{Raman(I,J)} \approx \left\langle \left(\alpha_{IJ} \right)^2 \right\rangle = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\varphi \int_{-1}^{+1} F\left(\psi, \varphi, \cos\theta \right) \left[T^t \alpha T \right]^2 d\left(\cos\theta \right) \qquad (4)$$

In eq. 4 F(ψ, φ, cosθ) is the so called **orientation distribution function**.
F(ψ, φ, cosθ) is subject to the normalization constrain with respect to the total number of scattering centers $\iiint F\left(\Omega\right) d\Omega = 1$. In a uniaxial system which contains molecules of cylindrical symmetry, $F\left(0,0,\theta\right) = F\left(\theta\right)$ independent of φ and ψ. $F\left(\theta\right) d\Omega$ represents the fraction of molecules whose axis is within the solid angle dΩ at an angle θ to the aligning direction.
In our case the population of chromophores undergoes an alignment process perpendicularly to the polarization vector of the interference beam by means of isomerization and reorientation cycles and the final orientation function depends only on the polar angle θ. In this approximation the orientation function can be written as the sum of even order Legendre polynomials[44,46,49]:

$$F\left(\theta\right) = \sum_{l=0,2,4} \left(\frac{2l+1}{2} \right) \left\langle P_l \right\rangle P_l \left(\cos\theta \right) \qquad (5)$$

this can be analytically expressed as:

$$F(\theta)=\left\{\frac{1}{2}\langle P_0\rangle+\frac{5}{4}\left(3\cos^2\theta-1\right)\langle P_2\rangle+\frac{9}{16}\left(35\cos^4\theta-30\cos^2\theta+3\right)\langle P_4\rangle\right\} \tag{6}$$

with the coefficients $\langle P_l\rangle$ being the order parameters and defined as: $\langle P_0\rangle=1$, $\langle P_2\rangle=\frac{1}{2}\left(3\langle\cos^2\theta\rangle-1\right)$ and $\langle P_4\rangle=\frac{1}{8}\left(35\langle\cos^4\theta\rangle-30\langle\cos^2\theta\rangle+3\right)\cdot$

Here, a grating can be described by a sinusoidal function with a phase $\delta=\frac{2\pi X}{\Lambda}$, with Λ being the period of the grating. An additional rotation R(β) about the Z axis takes the different position over the grating into account. Then the Raman intensity will be proportional to[34]:

$$\langle\alpha_{IJ}^2\rangle=\left\langle\left[R(\beta)\left[T\alpha T^t\right]R^t(\beta)\right]^2\right\rangle \tag{7}$$

This allows the calculations of the intensities ratios $R_1(\delta)=\frac{I_{YX}}{I_{YY}}$ and $R_2(\delta)=\frac{I_{XY}}{I_{XX}}$, with the following analytical expressions[34]:

$$R_1(\delta)=\frac{\left\{\left(0.75\sin^2\delta\right)+\left(4-7.5\sin^2\delta\right)\langle\cos^2\theta\rangle+\left(8.75\sin^2\delta-4\right)\langle\cos^4\theta\rangle\right\}}{\left\{0.75\left(\cos\delta+1\right)^2+1.5\left(3-2\cos\delta-5\cos^2\delta\right)\langle\cos^2\theta\rangle-0.25\left(13+10\cos\delta-35\cos^2\delta\right)\langle\cos^4\theta\rangle\right\}} \tag{8}$$

$$R_2(\delta)=\frac{\left\{\left(0.75\sin^2\delta\right)+\left(4-7.5\sin^2\delta\right)\langle\cos^2\theta\rangle+\left(8.75\sin^2\delta-4\right)\langle\cos^4\theta\rangle\right\}}{\left\{0.75\left(\cos\delta-1\right)^2+3\left(1.5+\cos\delta-2.5\cos^2\delta\right)\langle\cos^2\theta\rangle-0.25\left(13-10\cos\delta-35\cos^2\delta\right)\langle\cos^4\theta\rangle\right\}} \tag{9}$$

When measuring the ratios R_1 and R_2, by means of (8) and (9), the averaged quantities $\langle\cos^2\theta\rangle$ and $\langle\cos^4\theta\rangle$ can be directly calculated and $\langle P_2\rangle$ and $\langle P_4\rangle$ derived.

Once the order parameters are known it is possible to infer what is the most probable distribution function consistent with the observed $\langle P_2\rangle$ and $\langle P_4\rangle$. In addition, we assume that the anisotropy in the system is produced in a smooth way, in other words without strong oscillations of the resulting orientation distribution. The "smoothest" distribution is taken as the best approximation to the "most probable" distribution.[44] In a statistical sense, the "most probable" distribution is the one in which the molecules are as randomly distributed as possible with the only constrain that the values of $\langle P_l\rangle$ are equal to the observed one. Thus, it is possible to calculate the distribution function $F(\theta)$ using information entropy. The entropy of orientation S of a distribution $F(\theta)$ is given by[43,44,50]:

$$S\left(F(\theta)\right)=-\int_{-1}^{+1}F(\theta)\ln\left(F(\theta)\right)d\left(\cos\theta\right) \tag{10}$$

Maximization of the information entropy by use of the Langrange multipliers method with constrains

$$\begin{aligned}\langle P_2\rangle&=\int_{-1}^{1}P_2\left(\cos\theta\right)F(\theta)\,d\left(\cos\theta\right)\\ \langle P_4\rangle&=\int_{-1}^{1}P_4\left(\cos\theta\right)F(\theta)\,d\left(\cos\theta\right)\end{aligned} \tag{11}$$

gives access to the distribution function $F(\theta)$

$$F(\theta)=Z^{-1}\exp\left[\lambda_2P_2\left(\cos\theta\right)+\lambda_4P_4\left(\cos\theta\right)\right] \tag{12}$$

where λ_2 and λ_4 are the Lagrange multipliers and Z^{-1} is a normalization constant:

$$Z = \int_{-1}^{+1} \exp\left[\lambda_2 P_2\left(\cos\theta\right) + \lambda_4 P_4\left(\cos\theta\right)\right] d\left(\cos\theta\right) \tag{13}$$

Polarized Raman imaging of surface grating relief

In Fig. 1S and 2S the results of polarization Raman imaging that refer to Fig. 7 in the article are shown together with typical spectra. The measurements of Fig. 1S are obtained when choosing the polarization vector of the Raman laser parallel to the grooves of the SRG. Fig. 2S displays the results when changing the polarization vector of the Raman laser by 90°, now perpendicular to the grooves of the grating. The images are obtained by evaluating the intensity of the peak centred at 1148 cm^{-1} ($\nu_{C\text{-}N}$). Analysis of different azo-group bands leads to similar results.

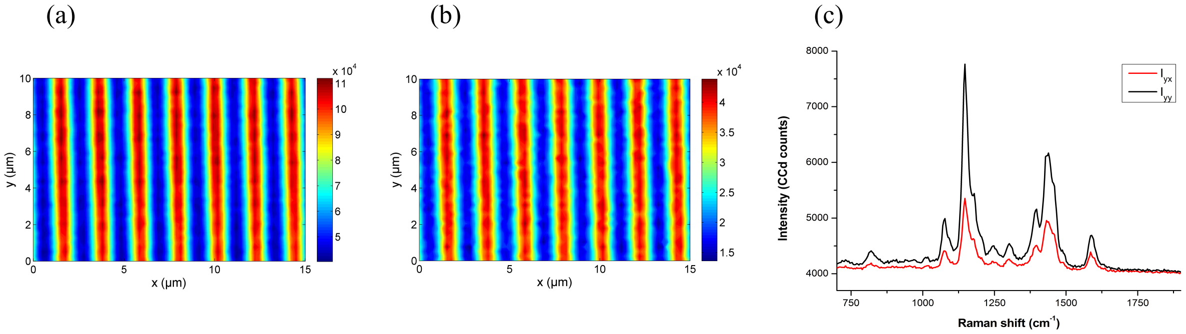

Fig. 1S Polarized Raman images: (a) intensity map I_{vv} (b) intensity map I_{vx}. (c) Polarized Raman spectra- I_{vv} and I_{vx}- in the 700-1900 cm^{-1} range

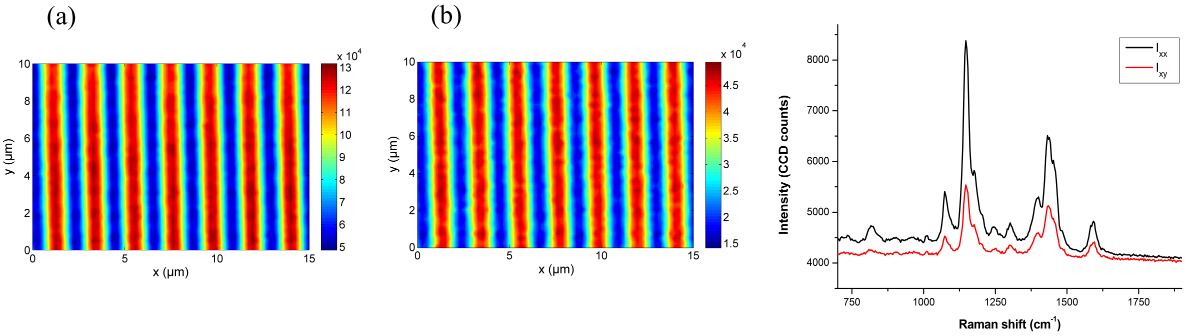

Fig. 2S Polarized Raman images: (a) Intensity map I_{xx} (b) Intensity map I_{xy}. (c) Polarized Raman spectra- I_{xx} and I_{xy}- in the 700-1900 cm^{-1} range. Spectra are taken at the top hill of the grating.

The Raman bands of the chromophores are polarized in both directions, parallel and perpendicular to the grooves of the SRG,, i.e. the cross polarized component of the Raman scattered intensity is less than the parallel component, thus allowing the calculation of the depolarization ratios R_1 and R_2. In Fig. 3S we present the relative intensities, i.e. the ratio $R_1 = I_{yx}/I_{yy}$ and $R_2 = I_{xy}/I_{xx}$ as calculated from the intensity maps of Fig. 1S and 2S.

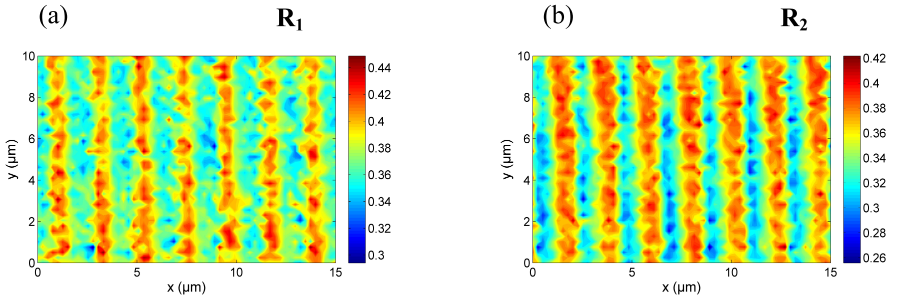

Fig. 3S Variation of the intensity ratios (a) $R_1(x) = I_{yx}/I_{yy}$ and (b) $R_2(x) = I_{xx}/I_{xy}$

Despite of the lower signal to noise ratio these images show a periodicity, however we notice a phase shift compared to Fig. 1S and Fig. 2S. In addition a phase shift of about π between R_1 and R_2 is also present.
In Fig. 4S the polarized Raman images referring to the scan reported in Fig. 8 in the article are presented. In both the experimental configurations the Raman maps show the usual features of the surface grating. The images of Fig. 2S, 3S and 4S show a clear periodicity, which reflects the topographic changes of the surface grating. The intensity variations are in phase with the relief as seen in the optical images.

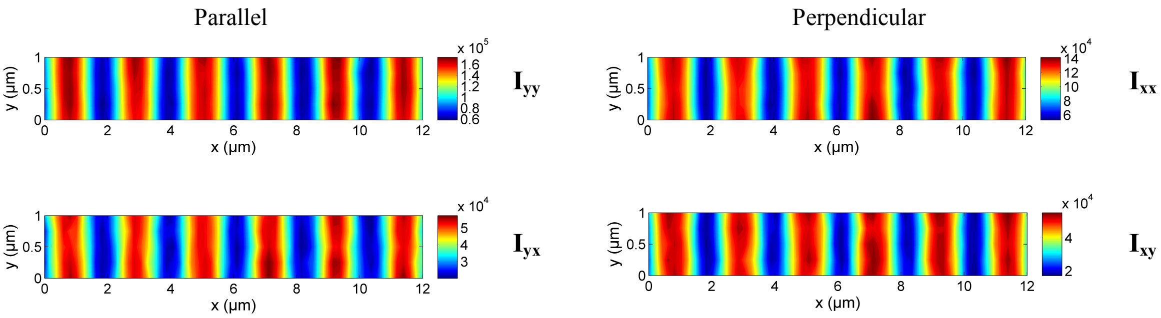

Fig. 4S Polarized Raman images measured with a polarization vector parallel and perpendicular to the grooves of the SRG.

Fig. 5S shows the orientation distribution functions obtained in three different regions of the grating: specifically at δ=0, 2π/5 and π in the usual cartesian representation showing only the first quadrant of the corresponding polar plot (cf. Fig. 15 of the article).

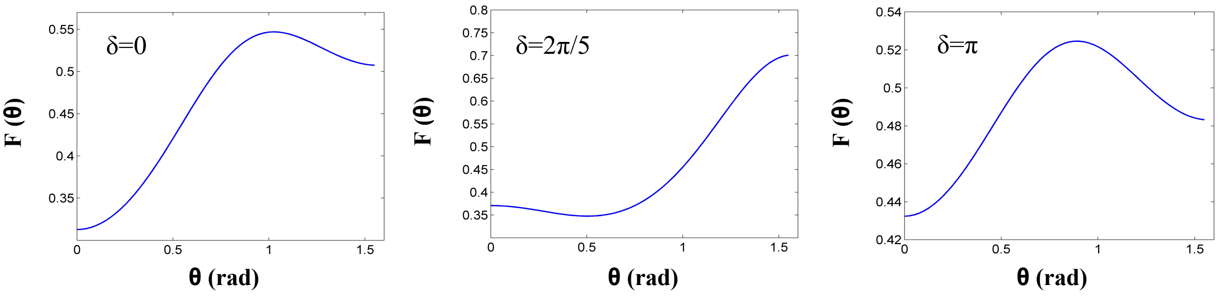

Fig. 5S Orientation distribution function F(θ) calculated at three different regions along the grating (the positions correspond to the grating phase equal to δ=0, 2π/5 and π)