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Determination of the Voigt constant of phthalocyanines by magneto-optical Kerr-effect spectroscopy

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Thin films of organic molecular semiconductors from the class of phthalocyanines are investigated by means of magneto-optical Kerr effect (MOKE) spectroscopy at room temperature. A numerical analysis of the energy dispersion of the real and imaginary part of the complex magneto-optical Kerr rotation angle in the visible to near ultraviolet spectral range allows the first determination of the magneto-optical material constant, the so-called Voigt constant, for a molecular material and the results are compared to density-functional theory calculations. The Voigt constant is only 1–2 orders of magnitude smaller compared with soft ferromagnetic materials such as Ni. The amplitude of the Voigt constant is exploited to determine the molecular orientation in thin films with high accuracy.

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I. INTRODUCTION

The interaction of light with matter belongs to the most fascinating natural phenomena, which allows to study the physical properties of the material under investigation in great detail. Measuring the state of polarization of an electromagnetic wave in the presence of an external magnetic field is one of the many possibilities used experimentally. The rotation of the light polarization upon transmission through a magnetized sample is known as the Faraday effect, and the change in the ellipticity as magnetic circular dichroism (MCD). The change in the polarization state induced by reflection on a sample under magnetic field is known as magneto-optical Kerr effect (MOKE).[1,2] These effects have their origin in the modification of the dielectric properties of the material in the presence of a magnetic field and can be described by a material parameter Q, the so-called Voigt constant, which occurs in the off-diagonal components of the macroscopic dielectric tensor. The quadratic magneto-optical Voigt *effect* plays no role in this paper, therefore "Voigt" always refers to the material parameter Q. When the magnetic field direction is parallel to the sample normal, defined as the z axis, the dielectric tensor has the following form:[3,4]

$$\underline{\varepsilon} = \begin{pmatrix} \varepsilon_x & iQ\varepsilon_x & 0 \\ -iQ\varepsilon_x & \varepsilon_x & 0 \\ 0 & 0 & \varepsilon_z \end{pmatrix}. \qquad (1)$$

The Voigt constant Q can be obtained from MOKE spectra recorded in polar geometry, as demonstrated in case of ferromagnetic films[5] with a thickness below the light penetration depth. The Voigt constant of ferromagnetic systems is usually of the order of 10^{-2}. Assuming that Q is known, a matrix formalism was developed by Zak *et al.*[3] in order to calculate magneto-optical effects of a multilayer system. This formalism describes the general case of an arbitrary magnetization direction of single layers and takes into account angles of incidence larger than zero.

Organic molecules that exhibit a very large penetration depth in the visible to ultraviolet spectral range were expected, given their paramagnetic nature, to have very low Voigt constants (of the order 10^{-6}–10^{-5}). Their magneto-optical activity is commonly probed via transmission measurements, by means of MCD spectroscopy. The MCD signal is correlated with the imaginary part of the complex Faraday rotation, which is given by[4]

$$\Theta_F = \theta_F + i\eta_F = \frac{\omega}{2c}\tilde{n}Qd, \qquad (2)$$

with ω being the angular frequency of the electromagnetic wave, c the velocity of light, and $\tilde{n}$ the complex index of refraction of the film with thickness d.

There exist numerous MCD investigations on organic molecules (see, e.g., Ref. 6 and references therein). MCD results can be used to verify theory assignments of the electronic states of the molecules.[7] However, for the determination of the Q constant from MCD spectra, the knowledge of the Faraday rotation is additionally required. The application of MCD is limited to molecular systems that are transparent in the investigated energy range and are either embedded in a transparent matrix or deposited onto transparent substrates. This may partially explain the lack of reports on the Voigt constant of organic molecular materials found in literature.

In this work we report the first determination of the energy dispersion of the magneto-optical Voigt constant for an organic molecular material deposited onto an opaque substrate in the visible to near ultraviolet range exploiting the sensitivity of spectroscopic MOKE measurements. A straightforward three-layer model to represent the air/organic film/substrate system is used to extract the Voigt constant from the MOKE spectra using as input parameters the optical constants, n and k, of the film and of the substrate as well as the film thickness determined from spectroscopic ellipsometry.

The class of phthalocyanines (Pc's) seems to be excellently suited for bench-marking the sensitivity and results of spectroscopic MOKE investigations on organic molecules since for many of its representatives—including copper ph-

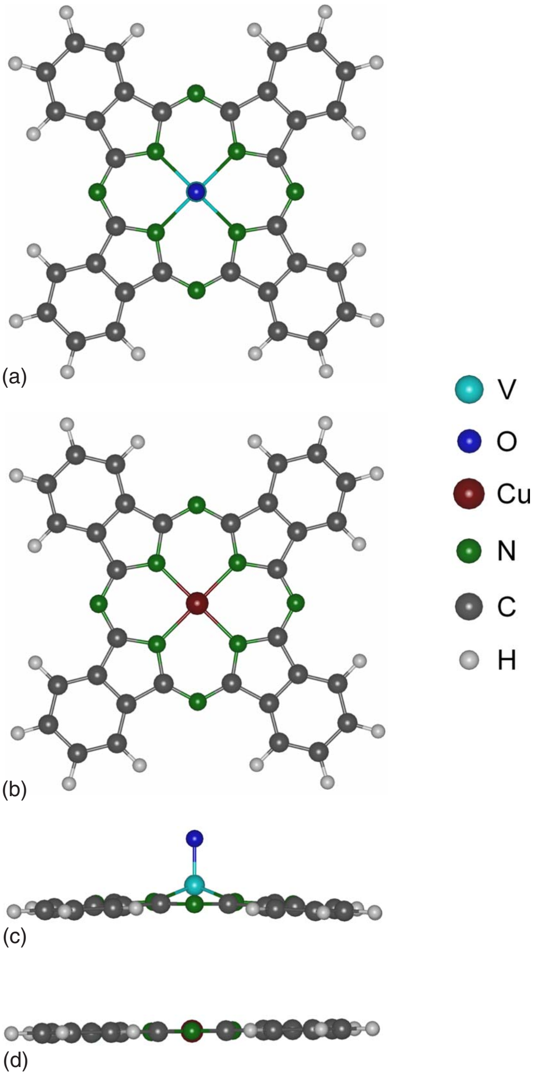

FIG. 1. (Color online) Schematic of the molecular structures of VOPc [(a) and (c)] and CuPc [(b) and (d)] in top and side view with the legend of the atom species.

thalocyanine (CuPc)—comparative MCD studies already exist.

Phthalocyanine molecules show semiconducting and photoconductor properties[8] and are often used as active layers in organic-based electronic or optoelectronic devices. In the view of possible applications in the emerging field of molecular spintronic devices, their magneto-optical activity in reflection mode when deposited on opaque substrates may be of great interest.

II. EXPERIMENTAL DETAILS AND THEORETICAL CALCULATIONS

The two phthalocyanine molecules investigated in this work, vanadyl phthalocyanine (VOPc) and CuPc (for the molecular structure see Fig. 1) have good thermal stability and are hence well suited for deposition of thin films by thermal sublimation in vacuum.

The VOPc layers were grown on Si(111) substrates covered with native oxide and on quartz substrates simultaneously, while the CuPc layers were deposited either on Si(111) substrates that were covered by native oxide (labeled as group 1) or Si substrates where the oxide was removed by dipping them in hydrofluoric acid (HF) followed by rinsing with de-ionized water (groups 2 and 3). The substrates used for the growth of the sample group 2 and 3 were dipped for 2 min in 40% HF and for 5 min in 5% HF, respectively. This procedure results in a H termination of the Si(111) surface. The etching in highly concentrated HF yields a considerably higher surface roughness then the etching in low concentration HF solution[9] and is expected to induce a standing orientation of the CuPc molecules[10] similar but not identical to the configuration on native oxide. On the smoother H-terminated Si substrates the molecules are tilted depending on the degree of remaining substrate roughness.

For each group, several films having different thickness were deposited under the same growth conditions. VOPc was grown with a deposition rate of (0.7 ± 0.1) nm/min at a base pressure of 2×10^{-6} mbar. CuPc was deposited with a rate of (0.20 ± 0.03) or (0.40 ± 0.04) nm/min at a base pressure of 8×10^{-6} or 5×10^{-8} mbar, respectively. According to our investigations, the effect of the base pressure at the used deposition rates on the molecular orientation is much smaller compared with the effect of substrate roughness.

The films grown on silicon and quartz substrates were investigated by means of MOKE spectroscopy and spectroscopic ellipsometry, and by MCD spectroscopy, respectively. All measurements presented here were performed at room temperature.

The MOKE measurements were carried out *ex situ* in a polar geometry with a home made setup similar to that described by Herrmann *et al.*[5] The magnetic field (0.35 T) is applied parallel to the sample normal and the light incidence angle is close to zero (1.3°). The sample is illuminated with *s*-polarized light. The setup measures the complex Kerr rotation $\Theta_K = \theta_K + i\eta_K$, where θ_K is the tilt angle of the main axis of polarization introduced by the reflection on the sample, and η_K the ellipticity. The sign of the MOKE spectra is defined following a sign convention often met in literature (see, e.g., Ref. 5).

Magnetic circular dichroism spectra were obtained using a homebuilt instrument consisting of a JASCO J-715 spectropolarimeter and an Oxford Instruments SPECTROMAG magnetocryostat. The spectra were recorded for an 80 ± 3 nm film grown on quartz substrate.

Variable angle spectroscopic ellipsometry measurements were performed using an ellipsometer from *J.A. Woollam Co., Inc.* Ellipsometry measures the quantities ψ and Δ which are related to the ratio of the effective Fresnel coefficients r for s- and p-polarized light by the expression,

$$r_p/r_s = \tan \Psi \exp(i\Delta). \quad (3)$$

In order to support the experimental findings by theoretical means we carried out electronic structure calculation based on density-functional theory (DFT) as implemented in the all-electron full potential linearized augmented plane-wave (FP-LAPW) method.[11] The geometrical structure used for the calculations corresponds to the α-CuPc crystal structure as determined by Hoshino *et al.*[12] The basis set included 408 valence states and additional 955 local orbitals which were used together with the Perdew-Wang exchange-correlation functional.[13] The Voigt constant as defined in [Eq. (1)] can be calculated directly from the elements of the dielectric tensor calculated using FP-LAPW.[14] The effective **k**-point mesh size used for Brillouin-zone integration in case of calculation of optical properties was 400 as defined by the Exciting[11] input. The effect of spin-orbit coupling and a magnetic field normal to the molecular plane has been included in the electronic calculations of the α-CuPc bulk crystal.

III. RESULTS AND DISCUSSIONS

A. Determination of the Voigt constant of Pc's from the MOKE spectra

The MOKE spectra shown in Fig. 2(a) are measured on three VOPc samples with film thicknesses of 40 ± 2, 58 ± 2, and 80 ± 3 nm. The main spectral features shift toward lower energies with increasing film thickness, an indication that they are strongly influenced by interference effects.[15] Therefore thin film (see, e.g., Ref. 5) or half space approximations (e.g. Ref. 1) are not applicable to these samples.

Ellipsometry measurements of the three samples were analyzed using a software package provided by the ellipsometer supplier[16] using a three-layer model air/film/substrate under the assumption that the optical constants of all three VOPc layers are the same. This allows to extract the optical constants (refractive index n and extinction coefficient k) and the thickness d of the films. The optical constants determined for the VOPc films are shown in Fig. 2(b).

The films were found to exhibit a uniaxial anisotropy of the optical constants, i.e., the values of n and k are different for light polarized parallel and perpendicular to the film surface [note the different magnitude of n and k in the upper and lower graphs of Fig. 2(b)]. For modeling the MOKE data only the optical constants for the in-plane polarization are relevant because of the nearly normal incidence in the MOKE setup.

The Voigt constant of organic films could be evaluated directly from the experimental data using the formalism presented in Ref. 3. In the present case, however, the problem can be simplified significantly, since the angle of incidence can be considered to be zero. The magnetization of a paramagnetic medium is always parallel to the magnetic field direction. In our setup the magnetic field is applied normal to the thin film and hence nearly parallel to the propagation direction of the light. Further simplification arises, because the investigated samples can be modeled as three-layer systems, two of the layers with infinite thickness (see Fig. 3 for a sketch). The incident light comes from the air side represented by a layer with infinite thickness and the refractive index $n_A = 1$. The second layer is the organic film with the thickness d and the optical constants known from ellipsometry investigations. Below the film the substrate is assumed to be a half space of silicon with 3 nm silicon oxide on top (if applicable) having effective optical constants as determined by ellipsometry. The latter assumption is reasonable because the thickness of the oxide layer is much smaller than the shortest wavelength of the light (225 nm).

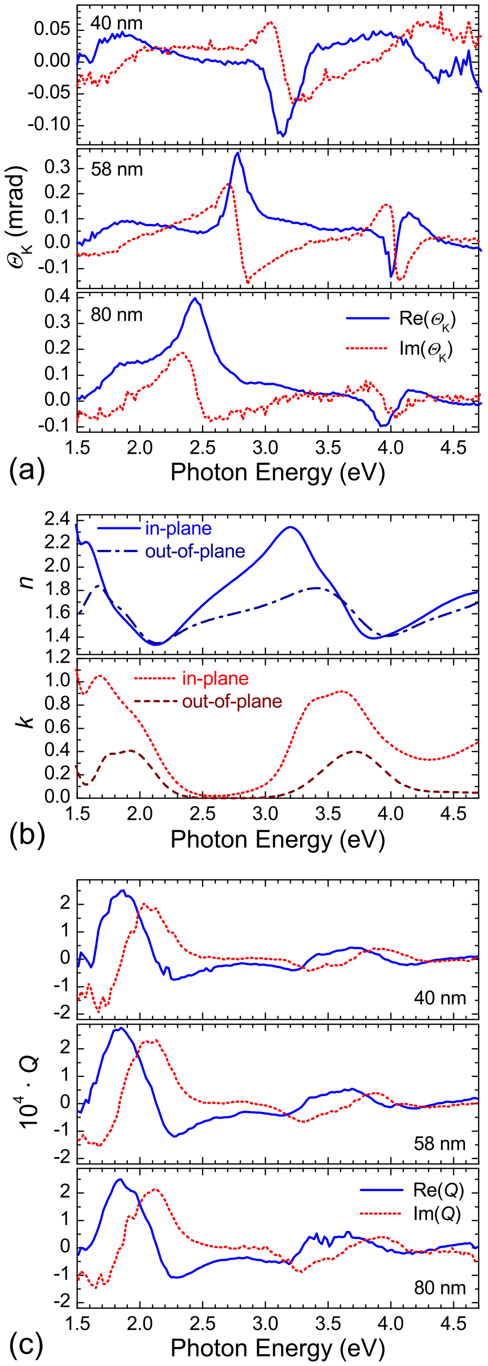

FIG. 2. (Color online) (a) MOKE spectra of three VOPc samples with different film thicknesses. (b) Optical constants of the VOPc films in the plane and perpendicular to the layer plane (out-of-plane). (c) Voigt constant Q extracted from the MOKE spectra and the optical constants.

The modeling of the MOKE spectra accounts for optical effects occurring at the interfaces between air and the organic layer as well as between the organic layer and the substrate and for the light attenuation in the organic layer.

In Fig. 3, t and r represent the Fresnel coefficients for light transmission through and reflection at an interface, respectively. In the case of normal incidence,

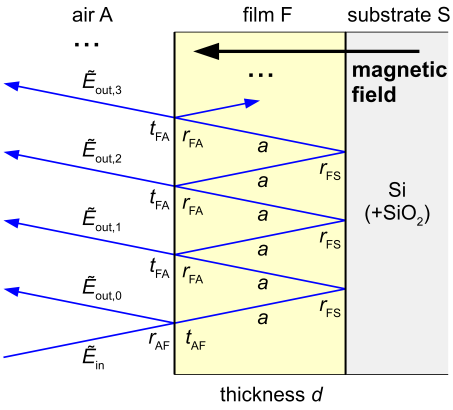

FIG. 3. (Color online) Sketch of the three-layer model. The Fresnel coefficients of the interfaces (r,t) and the propagation terms (a) in the organic layer are marked. The sketch holds for each of the two circular polarization states of the light, and the electric field vectors of the outgoing radiation, $\tilde{E}_{\text{out}}$, are summed up separately for each of the two circular polarization states. For a better visualization the angle of incidence is shown to be larger than zero in the sketch, while the model is constructed for the case of normal incidence.

$$t = \frac{2\tilde{n}_1}{\tilde{n}_1 + \tilde{n}_2} \quad \text{and} \quad r = \frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2}. \tag{4}$$

The complex index of refraction $\tilde{n}=n+ik$ is denoted with the index "1" for the medium where the light comes from or "2" for the one the light is going to or reflected on.

The term denoted by a stands for the exponential attenuation of light passing through the organic layer,

$$a = \exp\left[i\left(\tilde{n}\frac{\omega}{c}d \right) \right]. \tag{5}$$

The effective reflection coefficient u of the sample is obtained after superimposing all the outgoing light beams,

$$u = r_{\text{LF}} + \frac{t_{\text{LF}} \cdot t_{\text{FL}} \cdot a^2 \cdot r_{\text{FS}}}{1 - a^2 \cdot r_{\text{FS}} \cdot r_{\text{FL}}}. \tag{6}$$

Since the magnetic field is applied normal to the sample surface and hence nearly parallel to the propagation direction of the light, the eigenmodes for light waves are circular polarization states. The incident light is linearly polarized and can be considered to be composed of two circularly polarized components with a certain phase relation. Therefore the effective reflection coefficient u [Eq. (6)] has to be calculated for both circularly polarized components independently, considering that the magnetic field modifies the complex refractive index as

$$\tilde{n}_{\pm} = \tilde{n}(1 \mp Q/2). \tag{7}$$

This equation can be obtained by diagonalization of the dielectric tensor under the assumption of small Q values $(|Q| \ll 1)$. The indices "+" and "–" describe the mathematical sense of the rotation of the electric field vector from the point of view of the receiver.

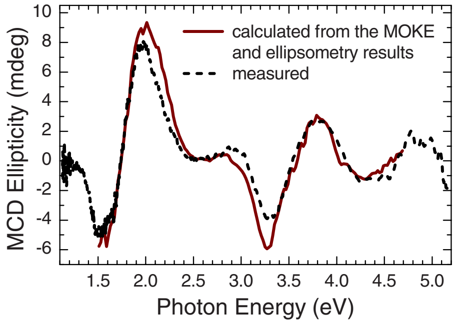

FIG. 4. (Color online) Comparison of a measured MCD spectrum (dashed line) for a 80 ± 3 nm thick VOPc layer on quartz at a magnetic field strength $B=0.35$ T with a MCD spectrum (solid line) calculated from the Voigt constant for a sample with the same thickness and at the same magnetic field strength.

Using the Jones formalism[17] the complex Kerr rotation Θ_{K} can be written as a function of the effective reflection coefficients for the two circular polarization modes $u_{\pm}$,

$$\Theta_{\text{K}} = \text{atg}\frac{i(u_+ - u_-)}{(u_+ + u_-)} \approx \frac{i(u_+ - u_-)}{(u_+ + u_-)} = f(\tilde{n}_{\text{substrate}}, \tilde{n}_{\text{layer}}, d, Q). \tag{8}$$

This equation can be solved numerically for Q if all other parameters are known from ellipsometry and MOKE measurements. To account for the sign definition of Q and the Jones vectors used here, the sign of the MOKE spectra needs to be inverted. The numerical calculations were performed using the MATLAB® software.

The dispersions of the Voigt constant resulting from the model calculations are shown in Fig. 2(c). As one can note, the interference effects are removed in the Q spectra, which provides support for our model assumptions.

For a further check of the model the calculated Q spectra and the optical constants were inserted into Eq. (2) in order to simulate the MCD spectrum of an 80 ± 3 nm thick VOPc layer at a magnetic field strength B of 0.35 T. In Fig. 4 the simulated MCD ellipticity (solid line) is compared with the experimental results (dashed line) obtained for an 80 ± 3 nm thick sample at the same field strength. The excellent agreement in the line shape and magnitude of the calculated and the experimental MCD spectra without any free adjustable parameter provides an independent proof of the proposed model. The small differences in the signal height in some spectral regions could be caused by slight structural differences in the VOPc films grown on different substrates (cf. the discussion related to CuPc). Please recall that the substrates of the samples measured by the MCD technique were quartz, whereas the layers for which the Voigt constant was determined were grown on silicon substrates. The similarity of the Q spectra in Fig. 2(c) shows that the magneto-optical behavior of the VOPc layers grown on the same substrate (Si) does not change significantly with the thickness in the range between 40 and 80 nm.

The Voigt constant of the CuPc samples was determined following the same procedure as described for VOPc. One exemplary MOKE spectrum is shown together with the cor-

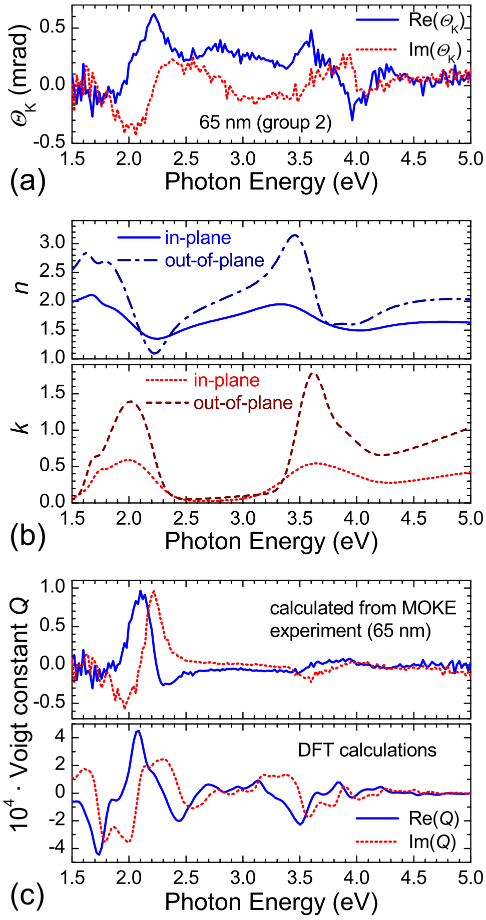

FIG. 5. (Color online) (a) Example of a MOKE spectrum of CuPc on rough H-Si. (b) Optical constants of CuPc on rough H-Si (they are the same on Si/SiO$_2$). (c) Comparison between the Voigt constants calculated from the experimental MOKE spectrum (a) and from DFT calculations.

responding optical constants and the Voigt constant dispersion in Figs. 5(a)–5(c), respectively. Using the Voigt constant of CuPc shown in Fig. 5(c), the MCD spectrum of CuPc was simulated and compared with MCD results from literature.[18] As in the case of VOPc, excellent agreement in the spectral line shape was found.

Further support that the CuPc Voigt constant obtained from the MOKE spectrum truly describes the properties of the molecular film comes from density-functional theory calculations. The Voigt constant has been obtained directly from the elements of the dielectric tensor calculated by means of the full-potential linear augmented plane-wave method using the bulk α-CuPc crystal structure[12] to model the thin film.

The electronic structure of pristine and potassium doped CuPc has very recently been discussed[19] with similar results as obtained here. The magnetic moment is localized on the Cu ion and the valence band is derived from Cu d states and π states of phthalocyanine. We did not try to correct our electronic structure by applying local Coulomb correlation as in LDA+U, therefore our band gap comes out too small, as is usual for standard DFT calculation. For that reason we shifted the calculated spectra by 1.25 eV to higher energies for better comparison with experiment as indicated in Fig. 5(c). In order to enhance the visual agreement between experiment and calculations we broadened the spectra by a running average. As shown in Fig. 5(c), there is reasonable qualitative agreement between the calculated and measured spectra.

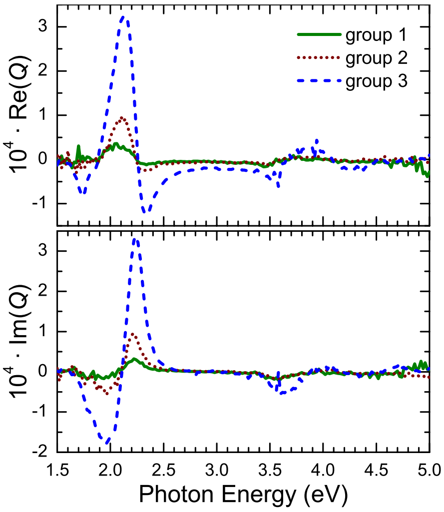

FIG. 6. (Color online) Dispersion of the Voigt constant of CuPc for three different groups of samples grown on differently treated Si substrates.

The large feature of the Voigt constant around 2 eV photon energy corresponds to the Q band observed in optical spectroscopy at the same energy and has the same origin ($\pi \rightarrow \pi^*$ transitions) as explained elsewhere.[20,21]

Both molecules investigated in this work, VOPc and CuPc, are paramagnetic with spin $\frac{1}{2}$. Investigations on metal free phthalocyanine and other diamagnetic molecular films showed that the presence of a nonzero spin in the ground state is, however, not crucial for the observation of a strong MOKE response,[22] in agreement with MCD findings. Of more importance appears to be the presence of a planar aromatic system, which enhances the response.

B. Dependence of the Voigt constant on the molecular orientation

Figure 6 shows the spectra of the Voigt constant obtained for three groups of CuPc films. All samples within one group can be described with the same Voigt dispersion. While the spectral shape is very similar, the magnitude of Q differs significantly for the three sample groups. The films grown on silicon covered with native oxide (group 1) exhibit the lowest intensity Voigt constants. The values of the Voigt constant of the CuPc films grown on silicon substrates which were H-passivated by 2 min dipping in 40% hydrofluoric acid (group 2) are about a factor of 2 larger than those of the films in group 1. The largest Q values are observed for the films grown on silicon substrates which were H-passivated by 2 min dipping in 5% hydrofluoric acid (group 3).

The main reason for the different intensities in the Voigt constants of samples grown on different substrates is suggested to be the orientation of the molecules in the films with respect to the substrate. The ellipsometry investigations

TABLE I. Values of the angle between the molecular plane of CuPc and the substrate plane estimated from the ellipsometry investigations. For a better comparison, column 3 and 4 provide the values of the cosine of the angle determined from ellipsometry and the magnitude of the Q constant at 2.1 eV normalized with respect to the corresponding value characteristic for the group 3.

CuPc layers	Angle α	$\cos(\alpha)$	Normalized cosine	Normalized Q magnitude
Group 1	$(85\pm4)°$	0.09 ± 0.07	0.15 ± 0.14	0.11 ± 0.03
Group 2	$(81\pm4)°$	0.16 ± 0.07	0.27 ± 0.15	0.25 ± 0.03
Group 3	$(55\pm4)°$	0.57 ± 0.06	1.00	1.00

showed a uniaxial character of the optical constants for all CuPc samples. However, the ratio between the in-plane and out-of-plane values of the optical constants differs between the three groups of samples. It was previously shown that the values of the extinction coefficient k in the spectral range of the Q band between 1.3 and 2.5 eV can be used to estimate the angle between the molecular plane and the substrate plane.[23] The procedure assumes that the Q band originates from two nearly degenerated optical transitions with transition dipoles lying in the molecular plane. Thus the single molecule can be considered to have disk symmetry in absorption and the angle α between the molecular and the substrate plane can be estimated from the ratio out-of-plane k to in-plane k using the formula,

$$\alpha = \arccos\sqrt{\frac{2A_{\mathrm{in}} - A_{\mathrm{out}}}{2A_{\mathrm{in}} + A_{\mathrm{out}}}} \tag{9}$$

with $A_{\mathrm{in,out}}$ being the in-plane and out-of-plane area in the extinction coefficient spectra of the Q-band range, respectively.[24] The angle estimated using Eq. (3) is given in Table I for each group of samples.

The influence of molecular orientation on the magneto-optical response has been discussed in Ref. 25 in order to extract information on the polarization of optical transitions in an isotropic molecular film from MCD results. There it has been suggested that two-dimensional (2D) transitions polarized in the molecular plane would produce a maximum MCD signal for light incident normal to the molecular plane and zero signal for light propagating parallel to the molecular plane. Consequently for light normal to the sample surface, perfectly lying molecules would yield a maximum MCD signal while standing molecules would give zero signal. Since the Q band of CuPc originates from two nearly degenerated optical transitions polarized within the molecular plane we assume that, in a first approximation, this hypothesis also holds for the Voigt constant. It must be kept in mind, however, that the exact angular dependence may differ compared to the case of MCD, because the angular dependent refractive index $\tilde{n}$ enters as a factor between Q and the MCD ellipticity [Eq. (2)].

Assuming a cosine dependence of the magnitude of Q on the molecular tilt angle, the magnitude of the Voigt constants of the sample groups 1, 2, and 3 should scale as 0.15:0.27:1 (Table I column 4). The ratio between the groups 2 (81°) and 3 (55°) can be found nearly exactly in the results (Table I, column 5). The intensity of the Q spectrum of the group 1 samples is only about 2/3 of the expected value. While at first glance this may appear to be a large deviation, we would like to stress that the deviation between the expected and observed intensity of the Q spectrum occurs in the case of samples where the molecules are almost standing on the substrate. Therefore the projection of the optical transition dipole moment on the substrate plane is small and consequently the cosine of the tilt angle is small and the relative error in its determination (e.g., from ellipsometry measurements) is large (0.15 ± 0.14). The observed deviation can easily be explained by a small error in the determination of the tilt angle of group 1 (e.g., 87.5° instead of 85°) from the ellipsometry measurements. Considering that the typical error in the estimation of the molecular tilt angle for ellipsometry investigations is ±4°, such a small difference of only 1.5° is hard to resolve from ellipsometry investigations alone. Therefore the MOKE measurements may provide a more sensitive tool to assess the molecular orientation.

IV. SUMMARY

This work demonstrates that several tens of nanometer thin films of paramagnetic organic semiconductors VOPc and CuPc exhibit a significant magneto-optical Kerr effect in the visible spectral range at room temperature. Their Voigt constant is found to be only about 2 orders of magnitude smaller than values reported for ferromagnetic layers such as Ni. Such strong magneto-optical activity of molecular thin films in reflection mode when deposited on opaque substrates may become of great interest in view of possible applications in the emerging field of molecular spintronic devices. Additionally, we demonstrated in the example of CuPc that the magnitude of the Voigt constant is highly sensitive to the orientation of the molecules with respect to the substrate plane. This opens new possibilities to accurately determine the molecular orientation in organic thin films.

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