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The optical absorption of ultrathin organic molecular films: the thickness dependence of the absorption line position

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Abstract. Thin films of copper phthalocyanine and of a perylene derivative have been deposited on NaCl and quartz glass. The effective thickness of these films ranged between approximately one monolayer and 50 nm. The films were prepared by thermal evaporation in ultrahigh vacuum. For ultrathin layers, we detected a blue-shift of the optical absorption bands of about 400 wavenumbers with respect to those of the corresponding bulk material. This shift is nearly the same for phthalocyanine and the perylene derivative. The shape of the absorption pattern is also thickness dependent. Additionally, model calculations have been performed to estimate the classical local field contribution to these shifting effects. The classical contribution was found to be of the order of the experimentally observed effect.

1. Introduction

The deposition of highly ordered molecular films by means of organic molecular beam epitaxy (OMBE) is a substantial branch of modern thin-film research; see for instance [1–4]. The motivations for this research are diverse; they extend from questions concerning fundamental aspects of the molecule–substrate interaction to concrete problems of applications such as electronic devices based on ordered organic layers. Both the preparation and the analysis of organic layers represent challenging experimental problems, because the organic materials may be destroyed by the techniques usually applied in inorganic solid-state experiments. Therefore, non-destructive analytical tools are especially important in the physics of organic layers, among them the methods of linear optical spectroscopy.

From the viewpoint of optical spectroscopy, the preparational efforts include at least two interesting research directions. The key point is that these ordered dye layers are usually very thin (with often less than 10 nm thickness), so their optical properties may be influenced by *both* ordering and dimensional effects, which are difficult to separate from each other. Thus ultrathin films (ordered as well as amorphous) often show absorption line positions different from those of the bulk materials. Accordingly, quite different mechanisms have been proposed to explain the observed behaviour, ranging from the increasing role of intermolecular interactions with increasing coverage [5] to exciton confinement effects in analogy to those observed in inorganic crystals [6].

In [7], we have already reported on experiments with copper phthalocyanine (CuPc) layers on fused silica. In that note, we reported an astonishingly good agreement between

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the observed absorption line shifts and the different spectral behaviours of the macroscopic dielectric function, which is responsible for the dielectric response of thick layers, and the microscopic polarizability, which should be responsible for ultrathin layers. The purpose of the present study is to investigate other material combinations to check whether or not this consistency was accidental.

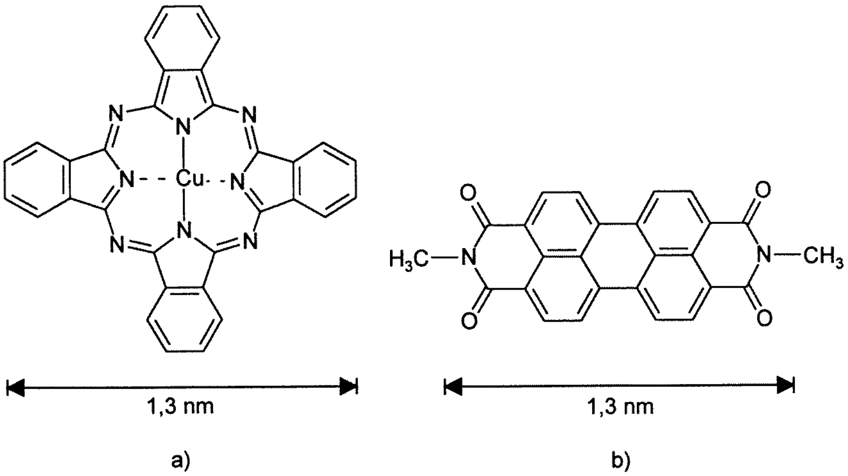


Figure 1. (a) Copper phthalocyanine (CuPc); (b) N, N′-dimethyl-3, 4, 9, 10-perylenedicarboximid (MPP).

Thus, we will investigate the dependence of the optical properties of different thin organic layers on the film thickness. No effort has been made to prepare ordered layers—the layers have been deposited by simple thermal evaporation on quartz glass substrates at room temperature and are expected to be polycrystalline. For comparison, a few layers have been deposited on NaCl. We focused our studies on the copper phthalocyanine (CuPc) as shown in figure 1(a)). In addition to the CuPc molecule, we investigated N, N′-dimethyl-3, 4, 9, 10-perylenedicarboximid (MPP) to test whether our results can be generalized. We have chosen MPP (as shown in figure 1(b)), because its symmetry is completely different from that of CuPc, although the two molecules are mutually comparable as regards their lateral extension.

2. Experimental details

2.1. Thin-film preparation

CuPc and MPP films were deposited on quartz glass (for optical measurements) and NaCl (for optical measurements and transmission electron microscopy, TEM) substrates by thermal evaporation in an UHV system designed for deposition of organic materials at a pressure of less than 5×10^{-10} mbar. First the substrates were cleaned in an ultrasonic bath with ethanol, and then they were annealed at 500 K for ten minutes in UHV.

Before evaporation, the commercially obtained organic dye powders were carefully purified three times by gradient sublimation in a high-vacuum device. Then the organic dyes were introduced into a Knudsen cell and degassed at about 10^{-8} mbar while the temperature was slowly increased from 300 K to 600 K. The deposition process was started at a substrate temperature of 300 K and a deposition rate of 1 nm min^{-1} at a residual gas

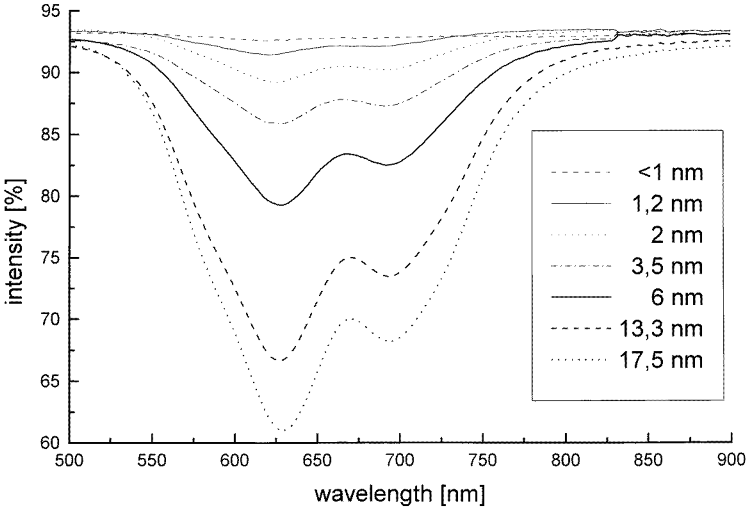


Figure 2. A section of the transmission spectra of CuPc on quartz glass for various film thicknesses.

pressure of about 5×10^{-8} mbar. The deposition rate has previously been calibrated by optical means, using *ex situ* optical thickness determination, from fits of transmittance and reflectance spectra of thick (above 50 nm) films [8].

2.2. Optical investigations

We have recorded normal-incidence transmission and near-normal-incidence reflection spectra of all samples in the photon energy range between 0.5 and 6.0 eV with a spectral resolution of 2 nm using a commercial NIR/VIS/UV spectrophotometer (Shimadzu UV 3101 PC). Aluminium mirrors and uncoated quartz glass substrates have been used as reflection standards.

The spectra of 'thick' films ($d > 5$ nm) have been evaluated, taking all multiple internal reflections into account (for a description of the method, see [8, 9]). For ultrathin adsorbate layers, where the average film thickness comes close to the film roughness (which is not exactly known, but should be expected to be in the region of a few nm), such a standard treatment does not make sense. In these cases we decided to identify the position of the absorption maxima directly from the transmission minima. In this (simplified) treatment, no reflections were taken into account. This simplification may cause errors [9, 10], which are in the range 1–2 nm in wavelength for the given material combinations for thickness values up to 20 nm, but are negligible for the ultrathin adsorbates. The thickness of these ultrathin films has been estimated from the (previously calibrated) deposition conditions. Additionally, an optical film thickness estimation has been performed, analysing the integral absorption in the full 0.5–6.0 eV photon energy region which gave similar results.

As regards the purpose of our study, the main aim was the identification of the position of the HOMO (highest occupied molecular orbital)—LUMO (lowest unoccupied molecular orbital) transition of the molecules. In the case of CuPc the first allowed electronic π–π^* transition, according to Gouterman's four-orbital model [11], is $a_{1u} \rightarrow e_g$ (the 'Q band').

As follows from the specifications of our spectrophotometer, the transmission measurement accuracy is of the order of 0.3%. Taking into account the electronic oscillator

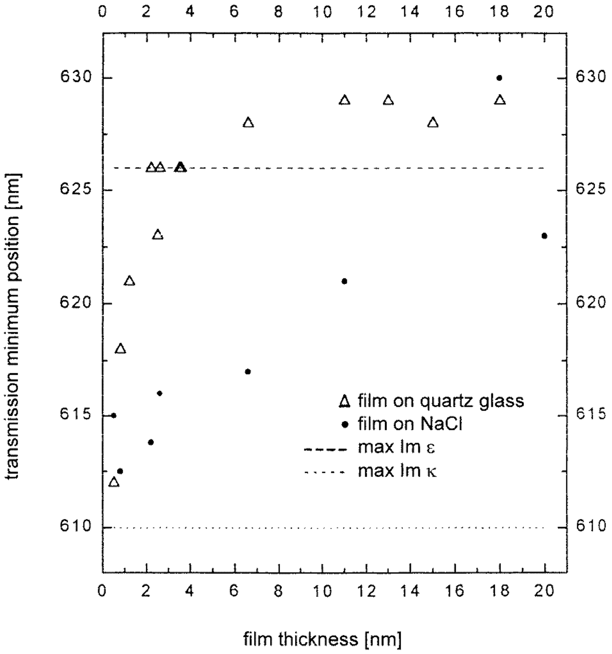


Figure 3. The shift of the transmission minimum position at around 625 nm for CuPc on quartz glass and NaCl substrates as a function of film thickness. Additionally, the maximum positions of the imaginary parts of the macroscopic dielectric function Im ε and the microscopic polarizability Im κ (see below) are shown as horizontal lines.

strength of the organic molecules (of the order of 0.2–0.5 for the transitions of interest [12, 13]) and their linewidth, this accuracy is equivalent to a detection limit of approximately 0.5 nm of CuPc on quartz glass. This is the lower limit of the thickness range investigated here. For MPP, we obtain a similar detection limit.

2.3. Transmission electron microscopy (TEM) investigations of films on NaCl

To perform transmission electron microscopy, the films were floated off the NaCl substrate in distilled water and transferred onto TEM specimen-supporting grids. The films having thicknesses of 6.5 nm and 10 nm were first coated with carbon films. The investigations were carried out in a CM20 FEG at an accelerating voltage of 200 kV.

As the samples on quartz glass are not accessible to TEM investigations, a direct comparison between optical and structural properties will be possible only for the samples deposited on NaCl.

3. Results

3.1. Optical investigations

Transmission spectra of the CuPc Q-band absorption region for various film thickness are shown in figure 2. Let us focus on the transmission minimum at around 625 nm. An examination of the minimum position leads to the dependence shown in figure 3 for fused silica and NaCl as the substrate. It is immediately seen that the CuPc layers behave

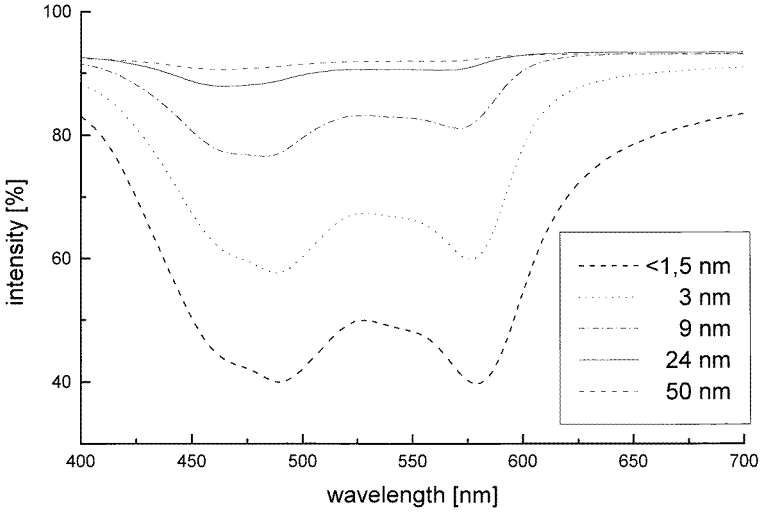


Figure 4. A section of the transmission spectra of MPP on quartz glass for various film thicknesses.

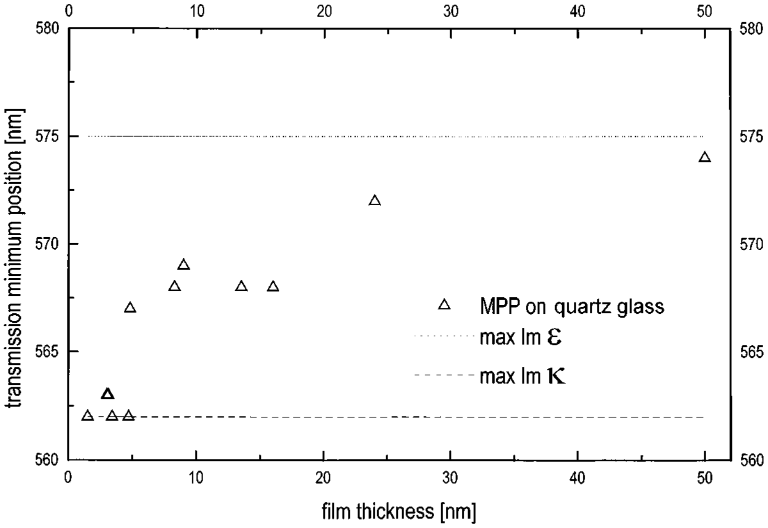
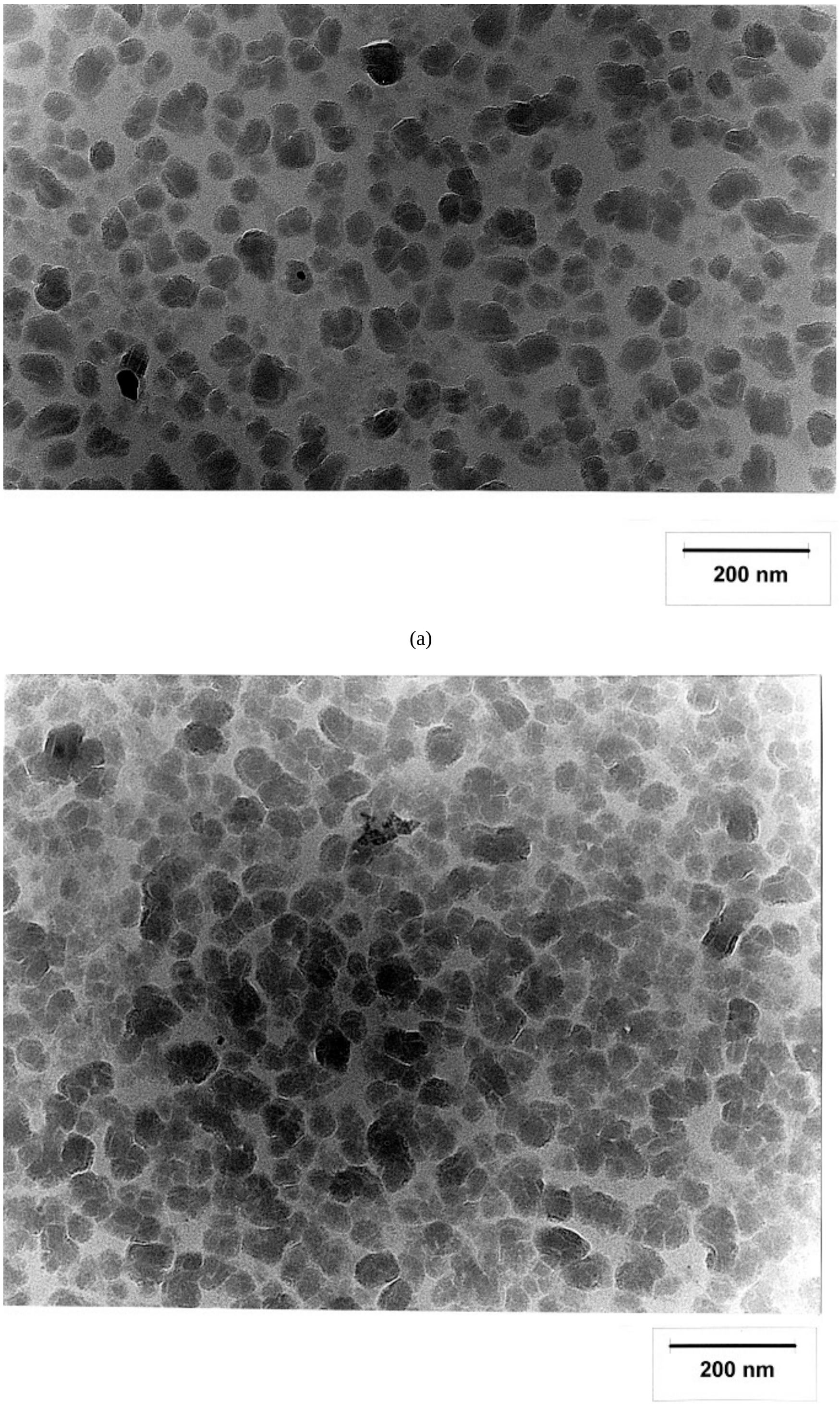


Figure 5. The shift of the transmission minimum position at around 575 nm for MPP on quartz glass as a function of film thickness. Additionally, the maximum positions of the imaginary parts of the macroscopic dielectric function Im ε and the microscopic polarizability Im κ (see below) are shown as horizontal lines.

differently on different substrate materials. While the peak shift for the sample on quartz glass sets in at a thickness below 5 nm, for the sample on NaCl we were already able to determine a shift while the thickness was still below 20 nm. The full shift values, however, are similar.

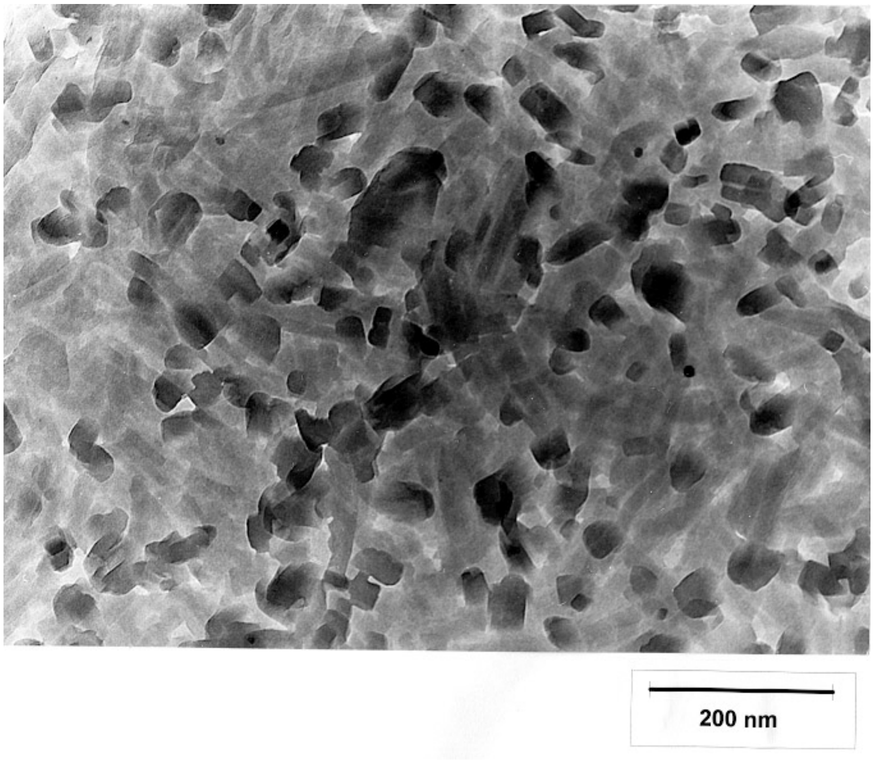
Figure 4 shows a section of the transmission spectra of the MPP films. Here we see a comparable shift of the transmission minimum at 575 nm. With decreasing film thickness



(a)

(b)

Figure 6. TEM images of CuPc on NaCl substrates (the deposition rate was 1 nm min^{-1}): (a) $d = 6.5$ nm; (b) $d = 10$ nm; (c) $d = 20$ nm.



(c)

Figure 6. (Continued)

the extremum positions generally shift towards the blue (see figure 5). The maximum shift is in the region of 16 nm in the case of CuPc and of 12 nm in the case of MPP. In terms of wavenumber units, the complete line shift of the transmission spectra below a critical thickness is approximately 400 wavenumbers for all three material combinations, while the ‘critical thickness’ for the line-shift onset is, however, strongly dependent on the chosen material combination.

The relative thickness error is of the order of a few per cent for the thickest layers and increases up to approximately 50% for the thinnest samples. Similarly, the absolute error of the transmission minimum determination has been estimated to be of the order of 1 nm for the thicker samples, while it is close to 4 nm for the thinnest samples, due to the decreasing absorption intensity.

3.2. TEM Results

Figure 6 shows the TEM images of CuPc films (deposited on NaCl) with average thickness values of 6.5 nm, 10 nm and 20 nm, respectively. The 6.5 nm film represents a film of isolated islands with lateral dimensions in the range 50–100 nm. This result confirms that thinner films are built from small islands which grow independently of each other, but may be influenced by the substrate. The same applies to the 10 nm film; however, the degree of substrate covering is considerably higher. The 20 nm film is closed and seems to be polycrystalline with a lateral size of the crystallites up to 200 nm.

4. Discussion

Regarding the results reported in the previous section, three main experimental facts may be stated.

(i) For all material combinations investigated here (CuPc on quartz glass, CuPc on NaCl, MPP on quartz glass), a blue-shift of the absorption structure in the region of the HOMO–LUMO transition energy as determined from the transmission minima is observed when the film thickness is decreased. In the thickness range investigated, the maximum shift value is nearly the same for all material combinations (around 400 cm^{-1}). It is not affected by the particular type of molecule and the corresponding electronic-vibrational structure of the absorption line investigated.

(ii) The 'critical' film thickness, at which this blue-shift starts to appear, differs for the three material combinations.

(iii) For CuPc layers on NaCl, the optical behaviour can be compared with TEM results. It turns out that the formation of a closed CuPc film (at 20 nm) is accompanied with the establishment of bulk-like optical properties of the CuPc layer, as seen from the Q-band absorption line position.

Generally, both classical and quantum mechanical effects may contribute to such line shifts. Possible quantum mechanical contributions are extensively discussed by several authors [5, 6, 14] in application to the same materials as we are dealing with (or similar ones). They may substantially explain the magnitude of the observed effects. The consideration of classical local field effects is more traditionally performed in application to inorganic film systems and, in particular, to cluster matter. The latter point seems to be especially interesting with regard to TEM pictures in figure 6. The aim of the following discussion is to estimate the *classical* local field contribution to the absorption line blue-shifts in phthalocyanine and MPP thin films.

Following the theoretical considerations in [15], the optical behaviour of ultrathin adsorbate films on a thick substrate should be determined by the behaviour of the microscopic polarizability of the adsorbate material, while for thicker films the macroscopic dielectric function is relevant. In terms of this assumption, it is the mismatch between the maxima of the imaginary parts of the dielectric function and the polarizability which forms the classical contribution to the line shift which would be observed for free-standing films. These local field ideas (with additional consideration of the field originating from the substrate surface) have successfully explained the observed absorption line shifts of argon adsorbate layers on metal substrates [16]. For our purposes it is therefore useful to study the frequency dependence of the dielectric functions and the corresponding polarizabilities.

For non-ferromagnetics, the dielectric function is the square of the complex index of refraction, so it immediately follows from the optical constants of the film materials. We determined the optical constants of thick CuPc and MPP films in the 0.5–6.0 eV photon energy region from transmission and reflection measurements [8]. Results are presented in references [7, 13] for CuPc and [17] for MPP. For CuPc, they are similar to literature data obtained using Kramers–Kronig data [18] and variable-angle spectroscopic ellipsometry [19]. Thus, the macroscopic dielectric function ε is easily accessible. In classical physics, it is connected to the polarizability κ via the relationship

$$\frac{\varepsilon - 1}{1 + a(\varepsilon - 1)} = N\kappa. \tag{1}$$

N is the particle density of the microscopic units (particles) characterized by the polarizability κ. Relationship (1) holds as long as the particle size is small compared to the wavelength of the light (the quasistatic regime). The depolarization factor a takes into consideration the optical anisotropy effects. In an isotropic case $a = 1/3$, and then equation (1) is identical to the Lorentz–Lorenz formula. For optically anisotropic particles, this depolarization factor declines from 1/3 and 'mediates' between the intrinsic anisotropy of the particle considered and the direction of the electric field strength vector. The values ε and κ have then to be understood as components of the corresponding tensors. For ellipsoidal particle shapes, the depolarization factors may be straightforwardly calculated [20]. Thus, for strongly oblate ellipsoids, the in-plane depolarization factor approaches 0, while the perpendicular one approaches 1. In contrast, for needles we have perpendicular depolarization factors near 0.5, while the parallel one comes close to 0. For our normal-incidence measurement geometry, it is therefore important to know the orientation of the particles with respect to the substrate plane.

Thus, detailed knowledge on the film structure would be necessary to accurately calculate the local field contribution to the observed line shifts. Lacking this information, we can only model special cases or estimate the maximum spectral shift by varying the depolarization factor a, keeping in mind that its maximum value is 1.

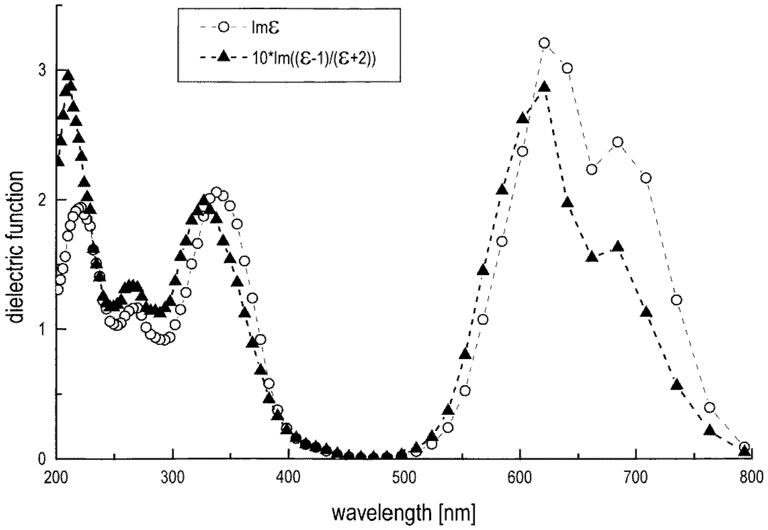


Figure 7. The dielectric function and polarizability dispersion for CuPc (imaginary parts only).

Figures 7 and 8 show the results of model calculations for the special case of an assumed optical isotropy ($a = 1/3$). For both materials, the imaginary part of the polarizability is blue-shifted with respect to that of the dielectric function, while the full shift value is of the order of 400 wavenumbers, close to the values observed in our experiments. This is also shown in the figures 3 and 5, where the corresponding maximum positions are marked. The calculated blue-shift is of course dependent on the assumed depolarization factor. It is useful to consider the possible extremal cases: for a depolarization factor close to zero, we will have no blue-shift at all, while for large depolarization factors close to 1, equation (1) predicts blue-shifts up to 700 wavenumbers for the absorption structures of interest. Moderate deviations from the optically isotropic case will result in intermediate depolarization factors, and in such cases equation (1) will ever yield blue-shifts of the order of a few hundred wavenumbers for optically anisotropic materials. This is the same

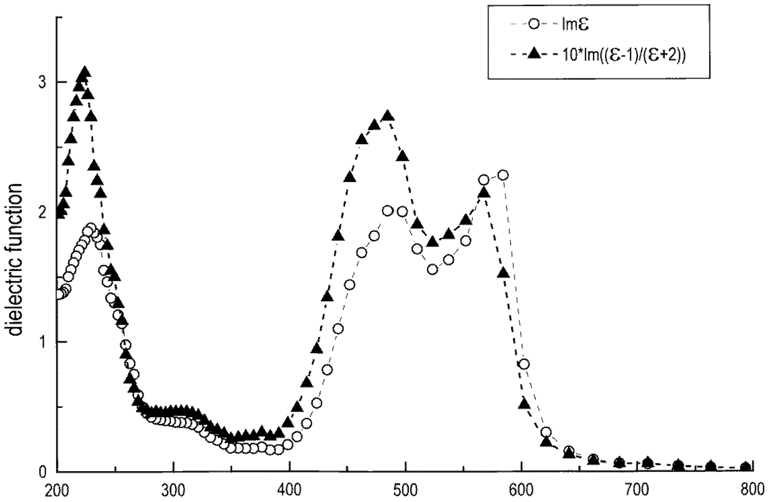


Figure 8. The dielectric function and polarizability dispersion for MPP (imaginary parts only).

order of blue-shift as is modelled in [6] in terms of a quantum confinement effect. It is therefore likely that local field effects are significant in this context and cannot be neglected in comparison with other effects contributing to such line shifts.

Consequently, this simple Lorentz–Lorenz treatment may substantially explain line-shift values being of the same order as those found in our experiments for a film thickness above 0.5 nm. In terms of this treatment, the similarity of the observed line shifts in the cases of the various material combinations appears as a consequence of the comparable non-resonant contributions to the dielectric functions of the different molecular film materials in the vicinity of their HOMO–LUMO transition.

There is another experimental point which may find an interpretation in terms of the local field treatment. On looking carefully at figure 4, one observes that the shape of the double structure in the MPP absorption pattern is thickness dependent. Here, with decreasing thickness, the structure around 480 nm becomes more pronounced. This thickness dependence is also reflected in the different shapes of the imaginary parts of the polarizability and the dielectric function (see figure 8). Indeed, the thinner layers tend to exhibit an absorption line shape similar to that of the polarizability, while that of the thicker layers resembles the dielectric function behaviour.

Concerning the ‘critical’ minimum thickness for obtaining bulk-like optical behaviour, the experimental data suggest that it may vary from material to material. Unfortunately, for the local field contributions, it seems impossible to unambiguously interpret the nature of this threshold. The problem is that the classical (quasistatic) polarizability concept—and consequently equation (1)—may find application in optics starting from atoms via molecules up to clusters of sizes of a few nanometre decades [21, 22]. Therefore, no unique length scale follows from the polarizability concept. For ideally smooth and homogeneous layers, one could assume that it is the fraction of surface molecules which must be negligible for bulk-like properties to form. Then, a few monolayers should be sufficient to achieve the bulk optical behaviour, which would predict a minimum film thickness of a few nanometres. This is essentially the situation which is discussed in references [15, 16].

The situation is more complicated for island growth. Then, it is rather the cluster interpretation of equation (1) which describes the local field contributions to the blue-shifts, and the latter appear as a consequence of the decreasing in-plane depolarization factor of the clusters (or islands) with increasing substrate coverage. Such an interpretation is applicable to the systems as shown in figure 6. An increasing CuPc average thickness results in more oblate islands (or longer needles) which in turn yield a line shift towards the bulk value. Additionally, the electrodynamic interaction between the clusters increases when the clusters are sufficiently close to each other. In terms of this interpretation, it is rather the film morphology which finally determines the observed critical thickness. For the situation sketched in figure 6, the obvious interpretation would be that the critical thickness is here determined by the percolation threshold.

In terms of this interpretation, the different 'critical' thickness values, where the line shifts become significant, may be determined by the specific growth conditions for organic materials on the substrates. For island growth (Vollmer–Weber), the critical thickness should be higher than in the case of monolayer-by-monolayer growth (Frank–van der Merwe), although the full shift value observed should be the same. We assume that the specifics of the intrinsic absorption line shift with increasing thickness may be used for a fast and non-destructive *a priori* estimation of the relevant growth mechanism. The intermediate situation of a rough but closed film is often discussed in terms of specially shaped clusters arranged on the surface of a closed film (see for example [23]) and thus represents a superposition of the above-mentioned special cases.

Summarizing the previous considerations, we state that classical local field effects may explain intrinsic absorption line shifts with increasing film thickness up to a value of a few hundred wavenumbers. This is the same order as obtained for related quantum mechanical contributions. However, they do not predict a unique critical thickness for the line-shift onset.

Another important question is that of the optical behaviour of the films in the submonolayer thickness region. Clearly, the limited sensitivity of transmission measurements prevented us from investigating the submonolayer thickness region here, and photoluminescence excitation spectroscopy is not suitable for copper phthalocyanine. For the MPP case, however, a photoluminescence excitation study [5] has recently been published, where corresponding line shifts have been observed for amorphous PTCDA and MPP layers with a nominal thickness ranging from 0.1 to 12 monolayers. The authors could distinguish two thickness regions in which the absorption maximum position variations with thickness were significantly different. For PTCDA, between 0.1 and 1 monolayer, a red-shift of almost 1000 cm^{-1} has been observed with increasing thickness, while between 1 and 12 monolayers a further (weaker) red-shift of 500 cm^{-1} could be identified. It has been suggested that different physical mechanisms are responsible for the spectral shifts observable in different thickness regions, involving nearest-neighbour interactions for ultrathin samples and interaction with molecules at larger distances for the thicker films, although no theoretical estimation of the expected magnitude of the line shifts thus caused has been given.

A comparison of these experimental findings with our results indicates that our layers show a behaviour similar to that of the thicker (amorphous) PTCDA layers of reference [5]. This is evident from both the thickness data and the wavenumber shift (400 cm^{-1} in our experiments, 500 cm^{-1} in [5]). Moreover, as the authors of [5] expect their molecules to 'feel' an isotropic environment in the amorphous films, the isotropic Lorentz–Lorenz treatment as discussed above should be applicable to their layers. As the thus-estimated classical local field contributions to the line shift are of a relevant order of magnitude, it seems likely that the 500 cm^{-1} shift identified in the thicker layers is partially caused by local field effects.

5. Summary

We prepared and investigated thin films of CuPc on quartz glass and NaCl, and thin films of MPP on quartz glass substrates. The thickness of these films varied from approximately one monolayer to a nominal thickness of 50 nm. The main aim of our investigation was that of investigating the dependence of the optical transmission behaviour on ultrathin film thickness. We determined a blue-shift of the absorption peaks when decreasing the thickness in all combinations of the organic dyes and substrates studied by about 400 wavenumbers. On the basis of the bulk optical constants, we estimated the classical local field contributions to the observed line shifts. It turned out that the value of the classical contributions is of the same order as the full line shift in the given thickness region and is thus not negligible. For the local field contributions, it is likely that the 'critical' average film thickness, at which the shift onset is observed, is influenced by the corresponding film growth mechanism.

Acknowledgment

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