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Electric Field Effects on Persistent Spectral Holes: Perylene in the Polar Polymer Polyvinylbutyral

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Abstract. We investigated the effects of an electric field on a spectral hole burned in the inhomogeneously broadened $S_0 - S_1$ transition of perylene in different samples of the polar polymer polyvinylbutyral (PVB) and in cellulose nitrate. The spectral hole is broadened and reduced in depth by the electric field. It was checked experimentally for perylene in PVB that the hole area remains constant when an electric field is applied. We determined the effective matrix-induced electric dipole moment differences $\Delta\mu^*$ for perylene in different PVB samples and in cellulose nitrate. Within experimental accuracy the value of $\Delta\mu^*$ is approximately independent of the composition of PVB and its water content. For perylene in cellulose nitrate the value of $\Delta\mu^*$ is larger by a factor of 1.5 than in PVB. The results are discussed on the basis of a simple model for the electric field effect.

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There have been several investigations of persistent spectral hole burning [1] in the $S_0 - S_1$ transition of the dye perylene in various matrices [2–6]. The application of an electric field [7–14] causes shifts of the electronic levels of the centrosymmetric perylene molecules, which depend linearly on the field strength, and changes the shape of the spectral hole. The electric field effects were found to be strongest for perylene in polar matrices [11, 13]. This is interesting not only for the study of the dye-matrix interaction but also for potential electro-optic applications [15–18] of spectral hole burning, including optical data storage in the electric field domain [15, 18].

Studies of the effects of an electric field on spectral holes of many other dye molecules [6–23] have shown that there is always a linear dependence of the electronic level shifts on the electric field strength, which is usually termed linear Stark effect. In non-centrosymmetric molecules this result has been attributed to the interaction of the electric field with the difference between the electric dipole moments of the excited and ground states of the dye molecules [9–12, 19–23]. In free centrosymmetric dye molecules like perylene the electric dipole moment difference is zero for reasons of symmetry. The observed linear electric field effect has been explained by the influence of the matrix on the dye molecules. The effect of a polar matrix is discussed in the literature [8–12, 19–22] in the following way. The matrix contains polar groups which produce an internal electric field. The internal field induces a dipole moment difference in the dye molecules, which interacts with the external electric field and causes the linear electric field effect. The matrix-induced electric dipole moment difference has to be taken into account also for the non-centrosymmetric dye molecules.

A commonly used matrix for studies of persistent spectral holes of dye molecules is the amorphous polymer polyvinylbutyral (PVB), which was originally used because thin films of excellent optical quality can be easily prepared [3]. PVB samples are amorphous, because the side groups of PVB, i.e. the acetal, ester, and hydroxyl groups, have different spatial dimensions and are statistically distributed along the polymer chain. In addition to perylene other centrosymmetric dye molecules, e.g. tetra-azoporphin [10], Zn-tetrabenzoporphin [19, 20] and octaethylporphyrin [21], and also non-centrosymmetric dye molecules, e.g. chlorin [9, 10, 19–21], resorufin, oxazine-4 and cresylviolet [22] have been dissolved in PVB matrices.

Recently, Gu and Hanson [14] investigated the electric field induced changes of spectral holes for perylene in PVB. They found that the reduction in depth of the spectral hole was more significant than changes in the width of the hole. For an explanation they presented a model of reversible spectral hole filling by the electric field which is based on field-induced tunneling in intrinsic two-level systems.

In this paper we present a detailed study of the effects of an electric field on spectral holes in the S_0-S_1 transition of perylene in PVB and in cellulose nitrate. For perylene in PVB our experiments showed, in contrast to the results of Gu and Hanson [14], that the spectral hole is broadened and reduced in depth, while the hole area remains constant, in agreement with model calculations [9–12, 19–21, 23]. Therefore, we determine the effective matrix-induced electric dipole moment difference $\Delta\mu^*$ of perylene in the usual way on the basis of these calculations. We found that the value of $\Delta\mu^*$ does not depend on the composition of PVB, i.e. on the concentration of the acetal, ester, and hydroxyl groups, and the content of water molecules. The value of $\Delta\mu^*$ for perylene in cellulose nitrate is larger by a factor of 1.5 than in PVB. The results are discussed in terms of a simple model for the interaction between the polar matrices and the perylene molecules.

1. Experimental

The perylene doped polyvinylbutyral (PVB) films were prepared in the following way. Perylene (Fig. 1a) and the polymer PVB (trade mark "Mowital", Company Höchst) (Fig. 1b) were dissolved separately in ethanol. The solutions were mixed in an ultrasound bath. One drop of the mixed solution was distributed on that side of a glass plate which was covered with an electrically conducting, transparent indium tin oxide layer (first electrode). The sample was dried for several hours in a box containing ethanol vapor. Then, an indium layer was evaporated in vacuum onto the PVB film, which was used as the second electrode for the application of the voltage. The PVB films had a thickness d of about 30 μm and a perylene concentration c of about 5×10^{-4} mol/l.

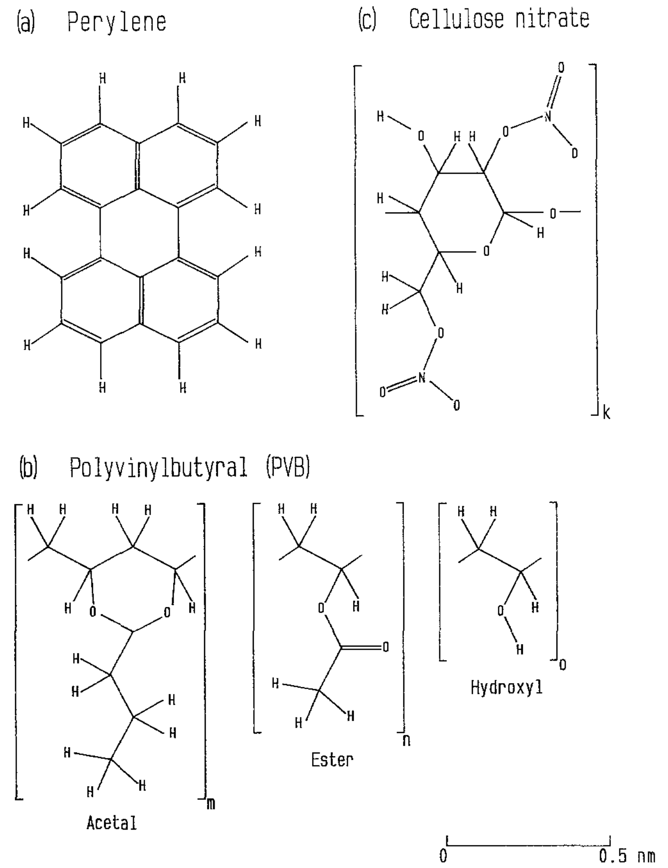

Fig. 1a–c. Molecular structure. **a** Perylene; **b** Polyvinylbutyral with acetal, ester, and hydroxyl side groups; **c** cellulose nitrate. All structures are drawn to the same scale

Cellulose nitrate (Fig. 1c) is a cellulose derivate where part of the three hydroxyl groups of the glucose unit are substituted by ONO_2 groups. In our samples, the average degree of substitution was about 2.2. The thin cellulose nitrate films were prepared in a similar way to the PVB

Table 1. Concentration by weight, χ, of the hydroxyl, acetal, and ester groups of PVB in different samples. Mowital is the trade mark of the company Höchst. Electric dipole moments m of the side groups of PVB, water, and the ONO_2 group in cellulose nitrate.

Polymer Group	m [10^{-30} Cm]	Mowital B60HH χ [%]	Mowital B60T χ [%]
PVB			
Hydroxyl	5.6[a]	14±2[e]	25.5±1.5[e]
Acetal	6.2[b]	83±2[e]	71.5±1.5[e]
Ester	5.6[c]	3[e]	3[e]
Water	6.1[d]	3±1[f]	7.6±2[f]
Cellulose Nitrate			
ONO_2	12.6[g]		

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[a] Electric dipole moment of the hydroxyl group in the alcohols methanol to buthanol. From [Ref. 24, p. E-65]

[b] Mean value of the electric dipole moments of three conformations of 1,3-dioxane, which has the same polar structure as the acetal group. From [Ref. 25, p. 169]

[c] Electric dipole moment of the ester group in CH_3OCOCH_3. From [Ref. 25, p. 91]

[d] [Ref. 24, p. E-64]

[e] Information sheet of the company Höchst

[f] Concentration by weight of water, determined in the way described in Sect. 1

[g] [Ref. 26, p. 90–224]

samples. But in the preparation procedure the polymer (trade mark Collodiumwolle, Wolf-Walsrode company, Germany) was dissolved in acetone instead of ethanol.

In the case of polyvinylbutyral we prepared different samples with and without water. We prepared films from the commercially available types of PVB, Mowital B60HH and B60T, which differ by the concentration of the acetal and hydroxyl groups while the concentration of the ester group is the same (Table 1 and Fig. 1b). Usually the PVB films contain an unknown amount of water. In order to remove the water as far as possible, the PVB films were heated in vacuum to 100° C for one hour, *before* the indium layer was evaporated onto the films. PVB samples prepared in this way from Mowital B60HH and B60T were termed for brevity PVB(HO) and PVB(TO), respectively.

We prepared also PVB samples with a definite amount of water in the following way. First, the PVB films were heated in vacuum to 100° C for one hour and the dried films were weighed. Then, the films were kept for several days in a box with saturated water atmosphere. After weighting the films again, the water content was calculated from the difference in weight. The PVB films made from Mowital B60HH and B60T contained 3% and 7.6% water, respectively. We term these samples PVB(HW) and PVB(TW). In order to avoid evaporation of the water from the PVB films during the evaporation of the indium layer, the samples were cooled with liquid nitrogen when the indium electrode was evaporated in vacuum.

The sample was immersed in superfluid helium in an optical cryostat at $T = 1.4$ K. The spectral holes were burned with an intensity of about 1 W/cm^2 for 1–10 s by a single-frequency dye ring laser (Spectra Physics, model 380D) with an external frequency stabilization. They were probed by fluorescence excitation spectroscopy with the same dye laser whose power was attenuated by a factor of 10^5. The maximum power of the dye laser was about 100 mW. Its wavelength was 441 nm. The frequency width of the laser light was less than 20 MHz. The frequency could be scanned automatically by 1 cm^{-1}.

2. Experimental Results

2.1. Determination of the Effective Dipolar Moment Difference of Perylene in PVB

The spectral hole was burned in the $S_0 - S_1$ transition of perylene in PVB without electric field. Then its changes by an electric field were determined for different electric field strengths. Figure 2a shows the measured spectral holes (points) for electric field strengths of $E = 0$, 2.9, and 4.4 kV/cm (curves 1, 2, and 3, respectively). Without electric field the width $\delta\bar{\nu}_H$ of the spectral hole is 0.027 cm^{-1}. The spectral hole broadens and reduces in depth when the electric field strength is increased. It is important to note that the area of the spectral hole remains constant within the experimental accuracy (about ±20%), independent of the electric field strength.

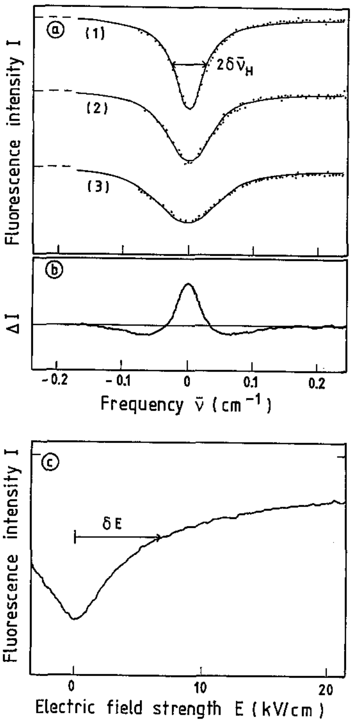

Fig. 2. a Spectral hole of perylene in PVB(B60HH) for different electric field strengths E: (1) 0 kV/cm, (2) 2.9 kV/cm, (3) 4.4 kV/cm. $\delta\bar{\nu}_H$ is the half width of the spectral hole without electric field. The solid lines are calcuated curves. **b** Difference between the spectral holes without and with an electric field applied to the sample ($E = 8.3$ kV/cm). **c** Fluorescence intensity in the center of the spectral hole versus electric field strength E. δE is the half width of the field hole

As described at the beginning, the electric field causes shifts of the electronic levels of the perylene molecules, which have been shown to be linear in the electric field strength. Since the dye molecules have different orientations and a different surrounding in the amorphous PVB matrix, there is a statistical distribution of electric-field-induced electronic level shifts which is responsible for the broadening of the spectral hole [8, 11, 19, 21]. In Fig. 2c the fluorescence intensity in the center of the spectral hole is plotted versus electric field strength E. It represents a hole in the electric field dimension (field hole) with a width $\delta E = 6.7$ kV/cm.

There is a problem which reduces the accuracy of the above measurements of the spectral hole in the electric field. During the probing of the spectral hole even the strongly attenuated power of the laser light causes slight hole burning, in particular in the wings of the hole. Therefore, it is difficult to determine accurately the area of the spectral hole.

In order to improve the accuracy of the determination of the electric-field-induced changes of the spectral hole we used another method. While tuning the laser frequency we applied a periodic sequence (frequency 3 kHz) of rectangular voltage pulses to the sample and used a lock-in amplifier to process the fluorescence signal. The lock-in amplifier measures the difference of the spectral holes without and with a voltage applied to the sample. Since

Table 2. Burning time t_B, spectral hole width $\delta\bar{\nu}_H$, field hole width δE, ratio $\beta = \delta\bar{\nu}_H/\delta E$ and effective dipole moment difference $\Delta\mu^*$ of perylene in PVB with different composition and water content and in cellulose nitrate

Matrix	t_B [s]	$10^3\delta\bar{\nu}_H$ [cm^{-1}]	δE [kV/cm]	β [MV^{-1}]	$\Delta\mu^*$ [10^{-30}Cm]
PVB(TO) without H_2O	1	44	12	3.67	0.90
	10	70	19	3.68	0.91
PVB(TW) 7.6% H_2O	1	30	7	4.29	1.06
	10	73	18	4.06	1.00
PVB(HO) without H_2O	1	27	6.7	4.03	0.99
PVB(HW) 3% H_2O	1	25	5.7	4.39	1.08
	10	47	11	4.27	1.05
Cellulose nitrate	1	122	12	10.2	1.53

the holes without and with voltage applied to the sample alternate rapidly (frequency 3 kHz), possible changes of the holes during probing are very similar without and with voltage applied to the sample. In this case, the measured difference between the holes, in particular in the wings of the holes, is much less affected by hole burning during probing than in the case of separate subsequent detection of the holes with and without voltage applied to the sample. Therefore, the accuracy in determining whether the hole area is constant is improved.

We measured the difference between the holes without and with voltage applied to the PVB sample for several values of the voltage. Figure 2b shows an example for a voltage of 24.9 V (electric field strength 8.3 kV/cm). In the center of the hole the difference is positive, while it is negative in the wings. This spectral dependence can be understood by subtracting curve 1 from curve 3 in Fig. 2a. Within the experimental accuracy (about ±8%) the integrals over the positive and negative parts of the difference curve in Fig. 2b have the same values, i.e. the area of the spectral hole remains constant when the electric field is applied.

Detailed calculations of the effects of an electric field on a spectral hole have been carried out in [8–12, 19–23]. Since the electric dipole moment difference of the free perylene molecule is zero for symmetry reasons, the observed linear electric field effect has been attributed to the influence of the PVB matrix. It can be described by introducing a statistical distribution of effective electric dipole moment differences $\Delta\mu^*$ in perylene. The most probable value $\Delta\mu^*$ of this distribution can be determined from the changes of the spectral hole in the electric field. In [12] the spectral hole shape was calculated for different electric field strength E under the assumption of a constant area of the hole. We fitted the results of these calculations [Ref. 12, Eq. 27] to the experimental curves of Fig. 2a. Best agreement between the calculated curves (solid lines) and the experimental points was obtained for an effective dipole moment difference of $\Delta\mu^* = 1.04 \times 10^{-30}$ C m for perylene in PVB. This quantity can also be determined from the widths $\delta\bar{\nu}_H$ and δE of the spectral hole for $E = 0$ kV/cm (Fig. 2a) and the field hole (Fig. 2c), respectively. Using [Ref. 11, Eq. 10] we get a value of $\Delta\mu^* = 0.99 \times 10^{-30}$ C m in good agreement with the value obtained from the fit shown in Fig. 2a.

We have determined the effective electric dipole moment difference $\Delta\mu^*$ for perylene in PVB for different angles γ between the electric field vector $\mathbf{E}_L$ of the laser light, which was linearly polarized, and the external electric field $\mathbf{E}$. The value of $\Delta\mu^*$ was constant within the experimental accuracy for values of the angle γ from 20° to 90°, as expected from the model calculations [12] for a centrosymmetric molecule like perylene.

2.2. Polyvinylbutyral of Different Composition and Cellulose Nitrate

We have investigated the effects of an electric field on a spectral hole for perylene in different PVB matrices and in a cellulose nitrate matrix. We measured the widths of the spectral hole and of the electric field hole, $\delta\bar{\nu}_H$ and δE. The ratio $\beta = \delta\bar{\nu}_H/\delta E$ is a measure of the strength of the electric field effect on the spectral hole. The effective electric dipole moment difference $\Delta\mu^*$ was determined in the two ways described in the preceding section: from the fit of the measured and calculated spectral holes and from the ratio β, using the relation

$$\Delta\mu^* = C\beta/f\,, \tag{1}$$

where the constant C has been calculated in [11]. The factor f relates the external electric field E applied to the sample to the local electric field E_l at the perylene molecules. In the Lorentz approximation we get

$$E_l = fE = E(\varepsilon + 2)/3\,, \tag{2}$$

where ε is the dielectric constant. The values of $\Delta\mu^*$ obtained from both methods agreed within the experimental accuracy.

The results for $\delta\bar{\nu}_H$, δE, β and $\Delta\mu^*$ for the different samples are shown together with the burning times t_B in Table 2. As expected, the burning time t_B has a strong influence on the widths of the spectral holes and the field holes, but not on the strength of the electric field effect, which is characterized by β or $\Delta\mu^*$. It is interesting to note that the effective electric dipole moment differences $\Delta\mu^*$

(and the ratios β) have the same values within the experimental accuracy ($\pm 20\%$) for perylene in the PVB samples of different composition and different water content. In contrast, the values of β and $\Delta\mu^*$ for perylene in cellulose nitrate are larger by a factor of 2.5 and 1.5, respectively, than the corresponding values for PVB.

3. Discussion

As mentioned above, both the ratio β and the effective dipole moment difference $\Delta\mu^*$ are a measure of the strength of the electric field effect on a spectral hole. However, the ratio β is obtained using the external field E applied to the sample, while the local electric field E_1 at the perylene molecule is involved in the calculation of $\Delta\mu^*$ [see (1)]. Since cellulose nitrate ($\varepsilon = 7.2$) has a much larger dielectric constant than PVB ($\varepsilon = 3.6$), its local field E_1 is stronger by a factor of 1.6 than that of PVB. This explains why $\beta_{\mathrm{CN}}/\beta_{\mathrm{PVB}}$ is larger than $\Delta\mu^*_{\mathrm{CN}}/\Delta\mu^*_{\mathrm{PVB}}$.

The following simple model [8–12, 19–22] is used for the discussion of the experimental results on the effective electric dipole moment differences $\Delta\mu^*$. The investigated matrices contain polar groups with permanent dipole moments m (Table 1) which produce an internal electric field E_i at the perylene molecules. The internal field induces an electric dipole moment difference

$$\Delta\mu^*_{(\mathrm{ind})} = \Delta\alpha \cdot E_i\,, \qquad (3)$$

where $\Delta\alpha$ is the difference between the polarizabilities of the excited and ground states of perylene.

E_i is the average internal field resulting from the superposition of the electric fields of the polar groups in the vicinity of the perylene molecules. In the point-dipole and point-polarizability approximations an asymmetric arrangement of the polar groups around the perylene molecules is required to get a large finite value of E_i. A symmetric environment could result in a zero average internal field. In general, the value of the internal field E_i in amorphous matrices is orders of magnitudes larger than the local field E_1. The local field E_1 describes the modification of the external electric field E by the matrix, while the internal electric field E_i is present without the external field E.

For the values of the effective electric dipole moment differences $\Delta\mu^*$ of perylene in PVB and in cellulose nitrate, the internal field E_i which is produced by the polar groups of the matrix is the dominant quantity, see (3). The electric dipole moments m of the acetal, ester, and hydroxyl groups of PVB and of the water molecule have about the same value, but are substantially smaller than that of the $\mathrm{ONO_2}$ group of cellulose nitrate (Table 1). If it is assumed that the $\mathrm{ONO_2}$ group is the dominant polar group in cellulose nitrate, a higher internal electric field and therefore a higher value of the effective electric dipole moment difference $\Delta\mu^*$ is expected as compared to PVB.

In the polar matrix PVB the concentration of polar groups is high, because every side group has an electric dipole moment. It can be seen from Fig. 1a and b, where perylene and PVB are drawn on the same scale, that each perylene molecule is close to at least one polar group. It appears reasonable that in this case saturation is approached. This means that further enhancement of the dipole concentration, e.g. by adding water molecules, will not substantially enhance the internal field E_i and therefore $\Delta\mu^*$. Our experimental results showed also that the value of the effective dipole moment difference $\Delta\mu^*$ of PVB is independent of the composition of PVB. This result can be explained in the model by the fact that the different side groups of PVB have about the same electric dipole moments.

An improved model should take into account that the internal electric field E_i produced by next neighbours is strongly inhomogeneous, i.e. the field strength varies considerably across the diameter of the perylene molecule (Fig. 1). Therefore, the point-dipole and point-polarizability approximations and the assumption of a homogeneous internal field E_i are not correct. In addition, it should be taken into account that changes, e.g. displacements and deformations, of the charge density distributions by the applied electric field can contribute to the electric-field-induced changes of the spectral holes.

Our results are consistent with the concept that the effective dipole moment difference $\Delta\mu^*$ is determined by the immediate neighbourhood of perylene. We suggest that the electric field effect of centrosymmetric dye molecules, like perylene, embedded in a complex matrix, e.g. in Langmuir-Blodgett films, can be used as a sensitive probe to get information about the immediate neighbourhood of the dye molecules.

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