Nonphotochemical Hole Burning Investigated at the Single-Molecule Level: Stark Effect Measurements on the Original and Photoproduct State

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By applying an external electric field, we have studied the dc Stark shifts at the two states of a low-temperature single-molecule optical switch. We observe a reversible change from a mainly quadratic field dependence to a linear field dependence. The data analysis provides the S_1-S_0 dipole moment and polarizability differences of both the original and photoproduct state. On the basis of these data, a detailed microscopic scenario for the underlying nonphotochemical hole burning mechanism is discussed.

Introduction

Persistent spectral hole burning has proven to be a sensitive high-resolution spectroscopic tool to investigate structural and dynamic properties of amorphous and crystalline solids at low temperature.[1] In the case of hole formation by the so-called nonphotochemical process, it is thought that the frequency-selective laser excitation leads to a change of configurational degrees of freedom in the nearby environment of the photoexcited centers or in the impurities themselves (or both).[2] The conformational states involved have been modeled as particular two-level systems that only change state upon light irradiation of the impurity. In general, detailed knowledge about the microscopic mechanism of the nonphotochemical process is rare. Methyl group spin conversion[3] and rearrangement of hydrogen bond networks[1] belong to the few mechanisms known in the literature.

Soon after the advent of single-molecule spectroscopy,[4,5] it became feasible to observe the hole-burning phenomenon at the single-molecule level.[6] In this case, the excitation line of a single molecule is shifted to a different frequency following light irradiation. For most systems, the new frequency position(s) and the time elapsed between the frequency jumps are not under the control of the experimenter. It has been shown recently that for the model system of terrylene in *p*-terphenyl these constraints are partially removed, thus allowing the switching of the resonance frequency of a single terrylene molecule in a controlled fashion by light irradiation.[7] Considering the exquisite sensitivity of a single absorber against changes of its local nanoenvironment, the ability to observe one single molecule at different frequency positions quite naturally leads to the important question of to what extent intra- and intermolecular interactions might differ at the various positions. Such studies also directly address the issue of nonphotochemical hole burning or more generally speaking of structural relaxation processes in solids. Similar experiments employing the more traditional population hole burning would be severely hindered by the generally much larger width of photoproduct antiholes. This broadening is a result of the lack of correlation between ensemble educt and product states and is a remainder of ensemble averaging still present in site-selective hole burning.

To get access to any measurable changes of physical parameters at the different spectral positions in a single-molecule experiment, it is necessary to apply a combination of complementary spectroscopic techniques. These might comprise fluorescence spectroscopy, hydrostatic pressure, or external electric fields, on which we will concentrate here. In recent single-molecule experiments, it had been found that a small spectral jump in the range of a few gigahertz was not accompanied (or caused) by a change of the linear Stark shift.[8,9] In the present paper, however, we will demonstrate that the huge light-induced spectral shifts of single terrylene molecules in *p*-terphenyl proceed along with a change of the Stark shift from predominantly quadratic to linear and vice versa.

Terrylene molecules embedded in crystalline *p*-terphenyl show four distinct, purely electronic origins at $T = 1.4$ K, which are denoted sites X_1-X_4 and thought to correspond to four different insertion geometries.[10] Chromophores belonging to the X_1 spectral site ($\lambda_{abs} = 580.4$ nm) allow controlled optical switching of single-molecule resonance lines;[7] prolonged resonant excitation of an X_1 molecule triggers a light-induced spectral jump to the photosite XY, during which the chromophore increases its absorption frequency by 843 ± 2 GHz. The intriguing aspect of this phenomenon is that the frequency jumps are fully reversible and that the overall behavior is found to be reproducible over a long time and from one sample to another.[7] The experimental evidence available so far indicates that the insertion geometry of terrylene in *p*-terphenyl is nonplanar with approximately D_2 symmetry and that the photoproduct states are characterized by changes in the matrix-induced distortion of the terrylene geometry.[7] A first hypothesis for the underlying mechanism argues that a degree of freedom known to exist in triclinic *p*-terphenyl, namely a flip-flop motion of the central phenyl ring of matrix molecules[11] adjacent to the chromophore, is most likely to open the reaction path to the photoproduct conformation.[7] These flip-flop motions are thought to be triggered in turn by conformational rearrangements[10] during the $S_0 \leftrightarrow S_1$ transitions of terrylene. The aim of the present work has been to improve the understanding of the

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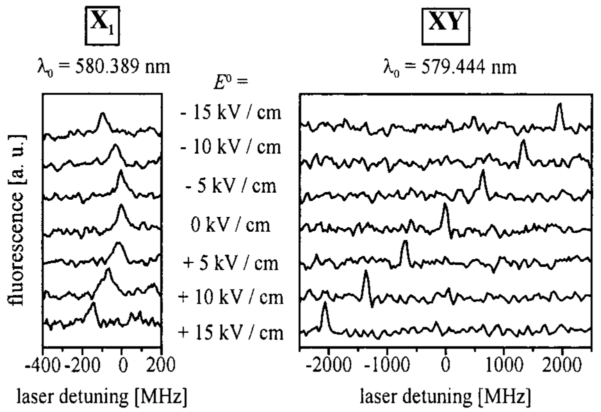

Figure 1. Spectral shifts of a single terrylene molecule induced by an applied electric field ($T = 1.4$ K). The left-hand side shows fluorescence excitation spectra of the absorber at its X_1 spectral position for different external field strengths $E°$, which are given in the middle column. The predominantly quadratic response can be discerned clearly. At the XY photosite, the same chromophore exhibits a different behavior that can be seen from the spectra on the right-hand side. A pronounced linear Stark effect is observed, and the overall sensitivity to the external field is much higher. (Please refer to Figure 2 and the text for a detailed analysis of the data presented here).

single-molecule hole-burning mechanism by probing dipole moment and polarizability changes with dc Stark spectroscopy.

Experimental Section

The samples used in our experiments were terrylene-doped platelets grown by cosublimation of terrylene and zone-refined *p*-terphenyl. These were mounted carefully between two glass substrates, each of which was coated with a layer of indium−tin oxide (ITO) on the side facing away from the sample to avoid charge carrier injection, and then integrated into a low-temperature SMS setup of the lens-paraboloid variety.[12] The Stark shifts were obtained from single-molecule fluorescence excitation spectra recorded for different external field strengths. This procedure is illustrated in Figure 1, which shows the field-dependent fluorescence excitation spectra of one terrylene molecule both for the original and the photoproduct state (sites X_1 and XY, respectively). A total of 15 molecules from three different samples were subjected to this measurement to make sure that the observed effect was reproducible and thus can be considered as characteristic for the light-induced frequency shifts.

Results and Discussion

All our experiments on terrylene in *p*-terphenyl clearly indicate that any mechanical strain exerted on the sensible crystal platelets immediately annihilates the "normal" terrylene insertion structure and the well-defined photophysical properties associated with it. Additionally, the concentration of the absorbers, which have to be considered as defects of the crystal structure, is best kept around $c = 10^{-10}$ mol/mol. As a criterion for uniform behavior, we checked the X_1−XY jump width, which was reproducibly found in the range of 843 ± 2 GHz if the crystal had been handled properly. Out of the investigated 15 molecules, only one exhibited a slight deviation of less than 1% (835 GHz). The fact that the results discussed below were uniform for three different samples validates the assumption that the observed effects constitute an intrinsic property of the configurational changes responsible for the spectral jumps and thus contain valuable mechanistic information. In a previous Stark experiment on terrylene in *p*-terphenyl,[13] the behavior was reported to be significantly less uniform and the characteristic X_1−XY frequency jumps were not observed at all. Therefore, no assignment of the molecular signals and the corresponding Stark shifts to the terrylene sites could be made.

The frequency shift $\Delta\nu$ of the $S_0 \rightarrow S_1$ transition of a molecule in a homogeneous electric field of strength $\mathbf{F}_a$ is given by the well-known relation[14]

$$h\Delta\nu = -\Delta\boldsymbol{\mu}\mathbf{F}_a - \frac{1}{2}\mathbf{F}_a\Delta\boldsymbol{\alpha}\mathbf{F}_a \qquad (1)$$

where $\Delta\boldsymbol{\mu}$ is the vector difference in the permanent dipole moments and $\Delta\boldsymbol{\alpha}$ is the tensor difference in the polarizabilities of the involved two states. The electrode setup used in the present work resulted in a homogeneous external field $\mathbf{E}^0$ that was nearly parallel to the *c* axis of the investigated *p*-terphenyl crystals. Therefore, it is a reasonable approximation to replace the inverse dielectric function of the medium ϵ^{-1} [15] by a scalar factor *f*, which relates $\mathbf{F}_a$ to $\mathbf{E}^0$ according to $\mathbf{F}_a = f\mathbf{E}^0$, thus neglecting the small anisotropy of the local-field tensor. This approach obviously also neglects the feedback effect of the induced guest dipole moment on the host matrix (the reaction field) but has already been successfully used to describe single-molecule Stark shifts.[8,16] Equation 1 is then reduced to a scalar equation where $\Delta\mu$ and $\Delta\alpha$ now correspond to the differences in dipole moment and polarizability, respectively, as seen in projection onto the direction of the applied electric field, which in our case was approximately parallel to the long axes of the chromophores and the *c* axis of the *p*-terphenyl crystal. Accordingly, a field correction factor of $f = 1.254$ was used, which is the *cc* component of the local-field tensor for monoclinic *p*-terphenyl.[17]

For molecules belonging to point groups where symmetry rules forbid the existence of a permanent molecular dipole moment (e.g., planar or D_2 symmetric terrylene), it has to be assumed that an observed $\Delta\mu$ must arise from an asymmetric dipole distribution in the surrounding host matrix, which amounts to a *permanent* local field $\mathbf{F}_p$[15] at the location of the guest. In that case, this permanent internal field of the host matrix can be probed locally by single-molecule Stark effect measurements. Application of this concept is problematic in the case of terrylene in *p*-terphenyl, however, because the measured $\Delta\mu$ can be expected to contain contributions from both the permanent local field of the matrix and the asymmetric distortions of the terrylene structure, which are hard to distinguish unequivocally from the data available so far. Therefore, the discussion below will be restricted to the parameters $\Delta\mu$ and $\Delta\alpha$ obtained from the Stark shifts by applying eq 1.

An example of the typical behavior can be seen in Figure 2, which shows the Stark plot obtained from the spectra shown in Figure 1. For the X_1 site, the Stark shift is predominantly quadratic, and an analysis according to eq 1 yields $\Delta\mu = +$-(3.5 ± 0.2) mD and $\Delta\alpha = +(2.1 \pm 0.1)$ mD/(kV/cm). When the same molecule visits the XY photosite, on the other hand, the behavior changes dramatically. An increased linear Stark shift now yields a dipole moment difference of $\Delta\mu = +(237 \pm 2)$ mD, which completely masks the quadratic contribution (indicating that $|\Delta\alpha| \leq 2.5$ mD/(kV/cm)). This impressive increase in the dipole moment difference was found for all investigated X_1 absorbers when they were sent to the XY site. It was observed that $\Delta\mu$ in X_1 can have opposite signs for absorbers located at different positions within the same crystal, which can most likely be explained to arise from the different, symmetry-related structural domains known to exist in triclinic

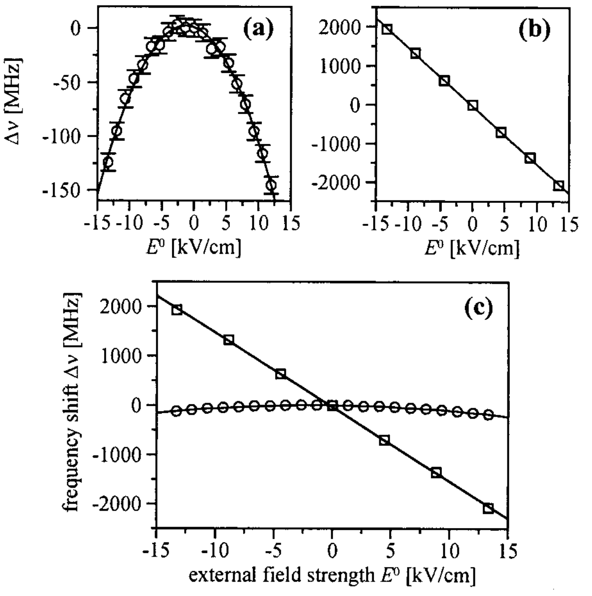

Figure 2. Stark effect measurement on a single terrylene molecule at sites X_1 and XY, represented by the frequency shifts $\Delta\nu$ as a function of the external field strength $E°$, as determined by fitting Lorentzian profiles to fluorescence excitation spectra of the absorber recorded for different external field strengths (the data shown here correspond to the spectra in Figure 1). Panel a depicts the data corresponding to the X_1 site (open circles with error bars and second-order polynomial fit), which yield $\Delta\mu = +3.5 \pm 0.2$ mD and $\Delta\alpha = +2.1 \pm 0.1$ mD/(kV/cm). Panel b shows the results for the same molecule in the XY photosite (open squares and linear fit), which correspond to $\Delta\mu = (+237 \pm 2)$ mD and indicate that $|\Delta\alpha| \leq 2.5$ mD/(kV/cm), since the quadratic component is masked by the increased dipole moment difference. Panel c shows the data from (a) and (b) unified in one graph so that the impressive change underlying the spectral jump can be fully appreciated.

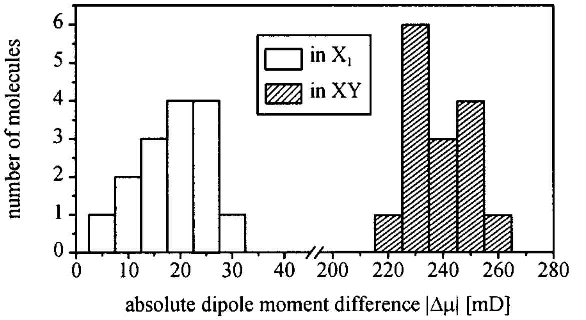

Figure 3. Observed absolute values of the S_1-S_0 dipole moment difference $|\Delta\mu|$ for 15 terrylene molecules in X_1 (open bars) and XY (hatched bars) at $T = 1.4$ K. The first moments of the distributions are $|\Delta\mu| = 19 + 7$ mD in X_1 and $|\Delta\mu| = 237 \pm 12$ mD in XY (please note the axis break).

p-terphenyl.[18] From the distributions of the absolute values of $\Delta\mu$, which are shown in Figure 3, we obtained $|\Delta\mu| = 19 \pm 7$ mD in X_1 and $\Delta\mu = 237 \pm 12$ mD in XY (mean value ± empirical standard deviation).

The small absolute values of $\Delta\mu$ in X_1, together with their large empirical standard deviation of about 37%, suggest that the dipole moments are induced mostly by the permanent internal field, which is influenced by randomly distributed matrix defects. They also support the assumption of a helicoidally twisted terrylene geometry (D_2),[10] which should exhibit no first-order Stark shift. In XY, on the other hand, the absolute values of $\Delta\mu$ increase by 1−2 orders in magnitude while their standard deviation decreases to about 5%. This indicates, in accordance with fluorescence spectra recorded in the photosites,[7] that a well-defined symmetry reduction of the terrylene molecules takes place that dominates over the effects of statistically distributed lattice imperfections.

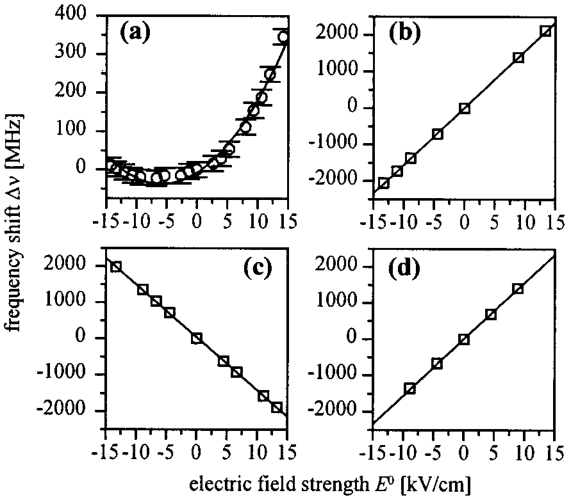

Figure 4. Changes in the single-molecule Stark effect for consecutive visits in the photosite XY ($T = 1.4$ K). Panel a shows the initial measurement in X_1, where a predominantly quadratic behavior was found, corresponding to $\Delta\mu = -16.3 \pm 0.6$ mD and $\Delta\alpha = -2.3 \pm 0.1$ mD/(kV/cm). Panels b − d depict the results of three measurements in XY, between which the absorber was sent to X_1 and brought back to XY by light irradiation. Linear fits to the data from panels b and d yield $\Delta\mu = -247 \pm 2$ mD, while for panel c one obtains $\Delta\mu = +231 \pm 2$ mD.

Another interesting observation was made when some absorbers were sent to photosite XY repeatedly; two chromophores (from different samples) were found to exhibit almost the same magnitude but different signs of the Stark shift $\Delta\nu$ (and correspondingly of $\Delta\mu$) for consecutive visits in XY. This behavior is illustrated in Figure 4. It is well-known from hole-burning spectroscopy in crystalline matrixes that chromophores with degenerate absorption frequencies can belong to subsets with different orientations of the dipole moments, leading to a splitting of spectral holes in external electric fields.[19] The novel result of the SMS experiments reported here is that we have experimental evidence for the existence of two “XY” photoproduct conformations for one and the same absorber, which give rise to approximately antiparallel dipole moment differences (with respect to the *c* axis) and result in the same absorption wavelength (measurement accuracy ±0.001 nm).

An additional peculiarity can be seen in Figure 4a. The quadratic contribution clearly shifts the resonance line toward higher frequencies with increasing external field strength, suggesting a negative value for the polarizability difference $\Delta\alpha$ if the data is interpreted according to eq 1. Perturbation theory predicts that the polarizability of a given electronic state is dependent on the transition dipole moments between this state and additional electronic states that have a similar energy and thus can yield strong contributions in the mixing of states induced by the external field.[14] Therefore, the excited state should always have a higher polarizability than the ground state, and consequently, the molecular $\Delta\alpha$ should be positive in all cases. The “anomalous” behavior exemplified in Figure 4a was only found in one of the three samples in which 75% of the chromophores exhibited negative values of $\Delta\alpha$. Since all molecules where investigated with the same straightforward technique, we think that a systematic experimental error can be ruled out. An explanation for this phenomenon might be the existence of structural defects in the crystal, which could lead to an increased local polarizability of the host lattice in the vicinity of the “anomalous” chromophores. In that case, the

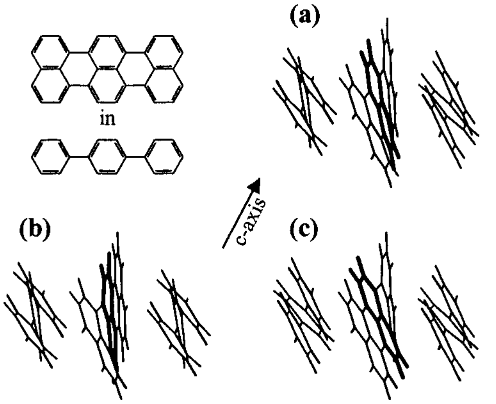

Figure 5. Microscopic scenario for the structural changes underlying the observed spectral jumps. Panel a shows the assumed X_1 conformation,[10] while panels b and c depict how a ring flip of either neighboring matrix molecule could affect the central naphthalene unit (bold) of terrylene, leading to the hypothetical photoproduct (XY) conformations. Please note that the terrylene deformations have been exaggerated in this schematic illustration.

interaction between induced dipoles can no longer be neglected as is done in the simplified approach on which eq 1 is based, and a more sophisticated description of the internal electric field in the crystal at an atomic level[20] as well as additional experimental work will be needed to extract the effective molecular polarizabilities. Nevertheless, we want to stress the fact that all of the “anomalous” chromophores showed the “normal” increase in $\Delta\mu$ when brought to the photoproduct state, which indicates that the well defined change of the dipole moment responsible for the spectral jumps dominates over whatever structural peculiarities might exist in the X_1 conformation of these absorbers.

On the basis of the data available we now want to propose a microscopic model for the nonphotochemical hole-burning mechanism of single terrylene molecules. Since the stability of mixed molecular crystals depends crucially on the structural match between guest and matrix, it has to be assumed that the host lattice is involved in the rearrangements leading to the spectral jumps. The degree of freedom in the *p*-terphenyl matrix considered likely to open the reaction path to the XY conformations is a central phenyl ring flip of a host molecule in the immediate vicinity of terrylene, as has been argued earlier[7] on the basis of a comparison with the spectral dynamics of pentacene in the same matrix.[11] Molecular packing calculations[10] indicate that two *p*-terphenyl molecules lie especially close to each impurity center so that they should most likely be affected by the repeated terrylene conformational changes accompanying the $S_0 \leftrightarrow S_1$ transitions. From central ring flips of these two molecules, a feedback effect on the chromophore can be rationalized that could tilt its middle naphthalene unit toward either one of the end units, as is illustrated in Figure 5. The asymmetric π conjugation resulting from this deformation can explain the increased dipole moment along the long molecular axis, and the two possible conformations depicted in Figure 5 can indeed be expected to yield antiparallel moments $\Delta\mu$ along the *c* axis. We have performed a ZINDO calculation[21] on a terrylene geometry where one end unit is tilted by 10° (see ref 10) against the common plane of the other two naphthalene units to see if the scenario described above is reasonable. This semiempirical treatment predicted a dipole moment difference between the ground and first excited state of $\Delta\mu \approx 270$ mD along the long molecular axis, which is in fairly good agreement with the measured values.

The last result suggests that the above model, while being somewhat intuitive, can serve as a basis for a more sophisticated approach that includes the matrix molecules and the reaction field. The experimental results additionally indicate that further Stark effect measurements on terrylene in *p*-terphenyl, performed with different directions of the external field, will provide additional insight into the single-molecule optical switching process.

Since the first days of single-molecule spectroscopy, a common cliché has been the notion of the accessibility of the local nanoenvironment of a single molecule. At the present stage, this nanoenvironment can be most successfully addressed not by investigating a static situation but rather by following or inducing changes of the surrounding that are reflected in the pertinent spectroscopic properties of the single absorber. It has been demonstrated in this paper that even more information can be extracted by the application of secondary spectroscopic techniques. As we have systems at hand that can be manipulated in a controlled fashion and allow long-term investigations, we are confident that the knowledge gained from such studies will ultimately serve to improve our understanding of structural relaxation in low-temperature solids and of the mechanism of inhomogeneous broadening in general.

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