

Tip-induced spectral dynamics of single molecules

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Received 20 November 2000

Abstract

Manipulation of spectral dynamics of single molecules (SM) by a metallized scanning probe tip is demonstrated. The Stark effect of the zero-phonon lines of single pentacene molecules in a *p*-terphenyl host at 1.8 K is investigated by applying a voltage to the tip in contact with the sample. The measured Stark shifts exhibit a plateau and the line widths depend on the electric field. These anomalies are explained by a model based on two-level systems with field-dependent double-well potentials. The experimental data show that the two-level systems are induced by the tip. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Experiments with single molecules (SM) at cryogenic temperatures have contributed significantly to the basic understanding of the low-temperature dynamics in crystals and glasses [1–4]. The narrow zero-phonon lines (ZPL) of single guest molecules are very sensitive probes for minute changes in their immediate environment. However, it is often difficult to relate the observed line shifts and broadenings to the actual microscopic mechanisms in the matrix. To shed light onto this problem the effect of external perturbations, such as pressure [5] and electric fields [6], on the ZPL frequencies of SMs has been investigated. More detailed insight is expected from well-defined local perturbers acting on SM spectral properties. This concept was realized, for instance, by using optically triggered matrix excitons [7]. Another

method is to use tips in order to impose local perturbations, such as stress and electric fields. Scanning probe technology in principle offers precise control of the tip positioning and of interactions. This way, specific properties of SM can be probed by perturbing their local environment. For example, tip-induced Stark shifts [8] and tip-induced lifetime changes [9,10] were investigated.

In this Letter we report first experiments on tip-induced spectral dynamics of SMs. We find that two-level systems (TLSS) activated by a tip lead to an anomalous Stark shift and a field-dependent line broadening of the ZPL.

2. Instrumentation and procedures

The setup consists of a sample-scanning confocal optical microscope for cryogenic operation [11] in combination with an *x*–*y*–*z* piezoelectric slip-stick drive for tip positioning. A tunable narrow-band ($\Delta\nu \simeq 1$ MHz) single mode ring dye laser operated at 16881.65 cm^{-1} is used to record SM excitation spectra. The sample was a 3–5 μm

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thick crystal flake at 1.8 K prepared by co-sublimation of *p*-terphenyl with a low concentration of pentacene. The crystal was attached to a cover glass by adhesion. By confocal imaging, a sample volume of $\approx 1 \mu\text{m}^3$ was selected that contained one or several spectrally separated molecules. A tapered optical fiber [12] coated with a 20 nm layer of gold was positioned close to the molecules. To approach and align the tip, HeNe laser light was coupled into the far end of the fiber. The positioning of the tip apex was controlled optically by observing the light emerging from the tip apex. After *x*-*y* positioning, the tip was approached to the crystal surface, possibly inducing a small, constant stress. Fig. 1 sketches the experimental configuration. For a fixed tip position excitation spectra were recorded for various voltages applied to the tip. To obtain more information about the influence of the tip on the observed effects we retracted the tip and recorded further spectra for the same but unperturbed molecules. Finally, the tip was inspected by optical and scanning electron microscopy. The shape of the tip was a cone with a 10 μm diameter plateau at the apex (see Fig. 1) and with metal only on the side. The truncated cone shape was a result of positioning procedures prior to the experiment and did not change afterwards.

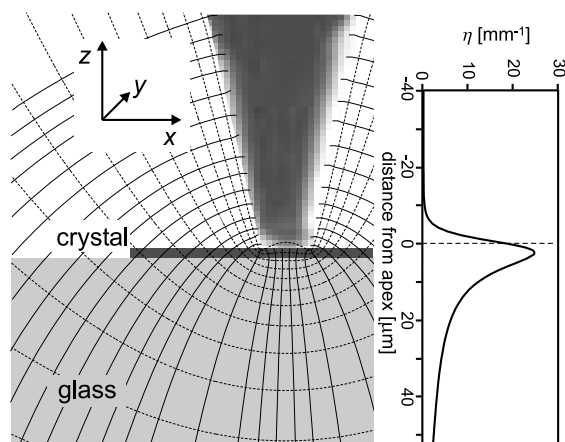


Fig. 1. Sketch of the experimental configuration: Optical image of the metallized tip with superimposed calculated equipotentials (dashed) and field lines (solid). Inset: electric field strength along the tip's symmetry axis for $U_{\text{ext}} = 1 \text{ V}$.

3. Results

We now discuss the spectra of two SM, M1 and M2, present in the confocal volume. 400 MHz frequency scans were recorded at 1.8 K, at an excitation intensity close to the saturation limit, and for a sequence of increasing voltages applied to the tip. For a tentative analysis of the ZPLs we fitted Lorentzians to the observed spectra. Corresponding ZPL peak positions and line widths are plotted in Fig. 2. The peak positions of both molecules are governed by the expected quadratic Stark effect [6]. In addition, the data reveal an anomalous behavior: (i) There are plateaus in the Stark shifts near zero voltage indicating a transition of the peak positions between two parabolas. (ii) At the position of the plateaus the lines are significantly broadened and the line shapes deviate clearly from Lorentzians (see Fig. 2). To exclude artifacts, we monitored the zero-field frequency positions during the experiment and we examined the area un-

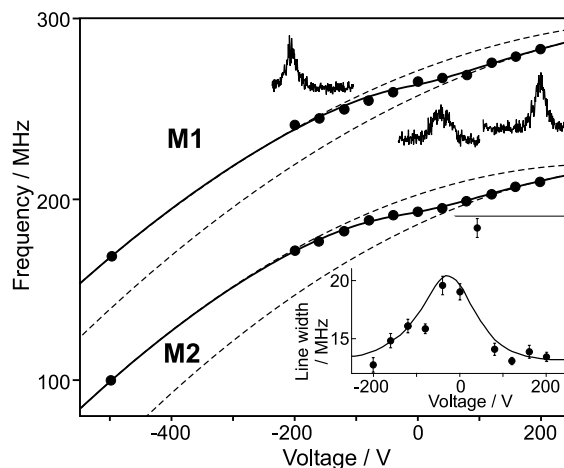


Fig. 2. Spectral positions of molecules M1 and M2 depending on the applied voltage. The dots denote the frequency positions of the ZPL determined from Lorentzian fits to the observed lines. The error bars are smaller than the symbol size. Representative line shapes are plotted for $\pm 200 \text{ V}$ and at the position of the plateau. The dashed curves give the predicted line positions for the two TLS states in the slow modulation limit. The full curves are the maximum intensity positions determined from the modeled spectra including the TLS dynamics. Inset: Linewidths of molecule M1 determined from Lorentzian fits. The continuous curve is the full width at half maximum determined from the computed spectra.

der the ZPL for the various voltages. Both quantities remained constant. This allows us to rule out laser drifts and power broadening as origins of the observed anomalies.

4. Discussion

To rationalize the observations, one has to assume that the electric field interacts not only with the SMs but also with additional mechanisms in the system which induce spectral dynamics. Usually, such mechanisms are modeled by tunneling TLSs [13]. These TLSs are coupled to the SM via strain or electric dipole fields. Upon flipping they induce jumps in the SMs transition frequencies. We have found that a model based on the presence of TLSs in addition to the Stark effect can account for the main features in the observed spectra. We assign a dipole moment μ_{TLS} to the TLSs which changes upon flips. Accordingly, the TLSs' double well potentials are modified when an electric field is applied [14]. As a result, the TLS-flipping rates and the equilibrium populations of their two states depend on the applied electric field strength. Consequently, also the spectral dynamics of the chromophores depend on the applied field. Spectral dynamics lead to deviations from the ideal Stark parabolas. Our observations indicate that here the spectral dynamics is dominated by a single TLS. The Stark shift may then be described by the usual expression [6,8] with one term added to account for the TLS's fluctuating electric field,

$$h\Delta v^{\pm} = -\frac{1}{2}\Delta\alpha f^2(E_{\text{ext}} + E_{\text{int}} \mp E_{\text{TLS}})^2, \quad (1)$$

where E_{ext} is the field owing to the applied voltage U_{ext} and E_{int} is the internal field due to the non-centrosymmetric arrangement of the host lattice and charges possibly trapped in the host. E_{TLS} is the field induced by the TLS dipole moment μ_{TLS} . $\Delta\alpha$ is the change of the molecular polarizability upon the excitation of the molecule. f is the Lorentz correction factor, an average value of $f = 1.254$ is used [15]. The plus–minus signs account for the two possible states of the TLS. In Eq. (1) all quantities are scalars. This simplified description nevertheless reproduces the main

features mentioned above, i.e., the two limiting parabolas. In combination with the TLS dynamics Eq. (1) also describes the observed transition between the two parabolas near zero voltage and the associated weakening of the Stark effect.

The electric field induced by the tip is strongly inhomogeneous. We calculated the field for the truncated cone shaped tip using a finite-element procedure, the result is shown in Fig. 1. We write for the external field $E_{\text{ext}} = \eta U_{\text{ext}}$, where η is given in units of inverse length: $\eta = \xi/L$, where $L = 1$ mm is the distance between the tip and the microscope objective serving as a counter electrode. ξ denotes the position dependent field enhancement as compared to planar electrodes. Because the position of the molecule with respect to the tip is not accurately known, only a range of the field enhancements can be given, $5 < \xi < 25$. In the following, the value of $\xi \simeq 10$ will be used as an estimate. Typically, for $U_{\text{ext}} = 100$ V applied to the tip, $E_{\text{ext}} \simeq 10$ kV/cm at the position of the molecule.

Eq. (1) describes two displaced parabolas, as shown by the dashed curves in Fig. 2. These parabolas correspond to the SM frequency positions in the slow modulation limit. In this limit, the contribution of the TLS to the SM line shape are δ -functions located at Δv^{\pm} . The mean and splitting of the two parabolas are given by $\overline{\Delta v} = \frac{1}{2}(\Delta v^{+} + \Delta v^{-})$ and $v = 2\pi(\Delta v^{+} - \Delta v^{-})$, respectively. Accelerated flipping dynamics of the TLS gives rise to a specific broadening of the SM line. The line-shape function in the time domain is given by [13]

$$\Phi(t) = \exp\left[-\frac{1}{2}(\Gamma_{\text{hom}} + K)t\right] \times \left[\cosh(\Omega t) + \frac{\theta}{\Omega} \sinh(\Omega t)\right], \quad (2)$$

where Γ_{hom} is the line width in the absence of the TLS. Furthermore, $\Omega = [(K^2/4) - (v^2/4) - i(p - 1/2)vK]^{1/2}$ and $\theta = (K/2) - i(p - 1/2)v$. K is the flip rate, $K = cJ^2\mathcal{E} \coth(\mathcal{E}/2k_{\text{B}}T)$, where c is the TLS-phonon coupling constant. \mathcal{E} is the TLS energy splitting, $\mathcal{E} = \sqrt{A^2 + J^2}$, where A is the asymmetry and J the tunneling parameter of the TLS. We noticed that generally $J \ll |A|$ so that $\mathcal{E} \simeq A$ and thus $K \simeq c'|A| \coth(|A|/2k_{\text{B}}T)$, where

$c' = cJ^2$ with c' as a dimensionless parameter. Finally, $p = 1/[1 + \exp(A/k_B T)]$ is the occupation probability of the upper state for $A > 0$ and of the lower state for $A < 0$. To account for the field dependence of the TLS, we write for the asymmetry $A = A_0 + 2f\mu_{\text{TLS}}E_{\text{ext}}$, recalling that μ_{TLS} is the dipole of the TLS changing its sign upon flipping. From Eq. (2) the line-shape function is cal-

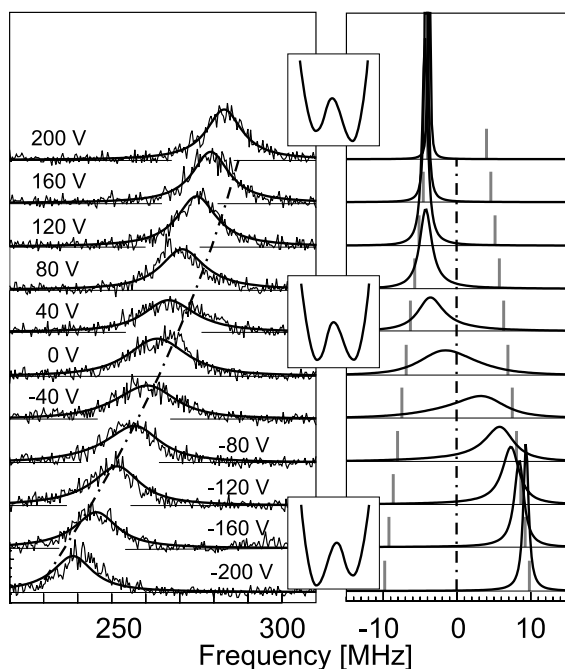


Fig. 3. ZPL of molecule M1 for a series of voltages as indicated. Left panel: Observed SM spectra with computed spectra superimposed. The dash-dotted line corresponds to the position of the line center $\bar{\Delta\nu}$. Note that the position of the intensity maximum relative to $\bar{\Delta\nu}$ changes with voltage according to the transition between the two parabolas. Right panel: Calculated line shapes for $\Gamma_{\text{hom}} = 0$ centered at zero frequency representing the contribution of the spectral diffusion to the line shape. Insets: sketches of the TLS double-well potential for -200 , 0 , and 200 V.

culated using complex Laplace ($t \rightarrow \omega$) transformation.

The parameters needed for a complete description of the system are: $\Delta\alpha$, E_{int} , and E_{TLS} for the two Stark-shift parabolas according to Eq. (1), A_0 , μ_{TLS} , and c' for the TLS dynamics, Γ_{hom} for the chromophore's homogeneous line width, and finally ν_0 as a global frequency offset. These parameters were determined by fitting simultaneously the calculated to all measured spectra. The parameters A_0 , μ_{TLS} , and c' , additional to the standard Stark parameters, are well determined by the distinct behavior of the line shapes. A_0 can be estimated from the voltage at the center of the plateau associated with the maximum in the line broadening. μ_{TLS} is related to the range of the line broadening anomaly in the inset of Fig. 2 and c' is related to the maximum broadening. The results of the fit are plotted in Fig. 3. The right panel shows the contributions of the TLS to the SM line shapes. It displays how the TLS equilibrium population changes as a function of the voltage. It also shows the expected linear narrowing of the TLS-induced splitting with increasing voltage due to the cross term $E_{\text{ext}}E_{\text{TLS}}$ in ν . At extreme voltages, the δ -function-like shapes indicate that the TLS is virtually frozen in one of the wells of the potential and does not broaden the SM lines. However, near zero voltage the accelerated flipping causes a broadening that contributes significantly to the SM line width. From the calculated spectra we determined the peak positions and the full widths at half maximum as a function of the voltage shown as solid lines in Fig. 2 and inset, respectively. With regard to the simplicity of the model, the agreement between simulations and observations is reasonable. The remaining small deviations indicate the presence of other TLSs that interact only weakly with the chromophores. The fitted parameters are listed in Table 1. The parameters

Table 1
Parameters determined from the experimental data

Molecule	$(\Gamma_{\text{hom}}/2\pi)$ MHz	$\Delta\alpha$ 10^{-39} Fm ²	E_{int} kV/cm	E_{TLS} kV/cm	A_0/k_B K	μ_{TLS} D	$c' = cJ^2$ 1
M1	12.4	1.3	-47	5.2	0.17	4.0	23
M2	11.1	1.6	-36	6.3	0.36	4.3	55

related to the parabolas are well defined while the TLS parameters depend on the details of the model. The resulting polarizabilities are compatible with previous SM measurements of $\Delta\alpha = 1.1\text{--}2.5 \times 10^{-39} \text{ Fm}^2$ [6] which corroborates our estimate of the field enhancement factor ξ . The observed internal fields are larger than the ones in [6] by a factor of 2 to 3. The stress induced in the crystal by adhesion to the cover glass may account for this difference. The strong dependence of the TLS flipping rate on the voltage results from a rather large dipole moment μ_{TLS} . If compared with $\mu_{\text{TLS}} \simeq 0.4 \text{ D}$ observed in hole-burning experiments in PMMA [14], the present values are larger by about one order of magnitude. This indicates that the microscopic nature of the TLS is presumably different here. From the values of E_{TLS} and μ_{TLS} we estimate the distance between the TLS and the chromophore to be about 5 nm. We speculate whether the TLSs could be due to charges which jump between two traps in the lattice. The large dipole moment justifies the model assumption that the TLS–chromophore interaction is by electric dipole fields.

With the tip retracted from the surface, further spectra were recorded to investigate the line position and broadening for the unperturbed molecules. The frequency position of molecule M2 did not change while the frequency of molecule M1 was shifted by 30 MHz. Taking known bulk pressure induced frequency shifts of 1 MHz/100 Pa into account [5] we estimate an upper limit for the pressure at the location of molecule M1 of 3000 Pa. This corresponds to a force of 240 nN exerted by the tip onto the surface. We varied the laser intensity to study the power broadening for the unperturbed molecules. The results are given in Fig. 4 where the linewidth Γ and the count rate R are plotted as $1/\Gamma^2$ vs. R . A linear fit and the corresponding 95% confidence region are also displayed. The linewidth at zero excitation intensity $\Gamma_0/2\pi = 7.6 \pm 1.9 \text{ MHz}$ and the saturation count rate $R_\infty = 127 \pm 9 \text{ counts/85 ms}$ are values typical for pentacene [16]. This, together with the small upper-limit force, is a strong indication that the crystal of *p*-terphenyl had not been damaged during the experiment. A selection of data from the tip-induced Stark experiment is also displayed in Fig. 4

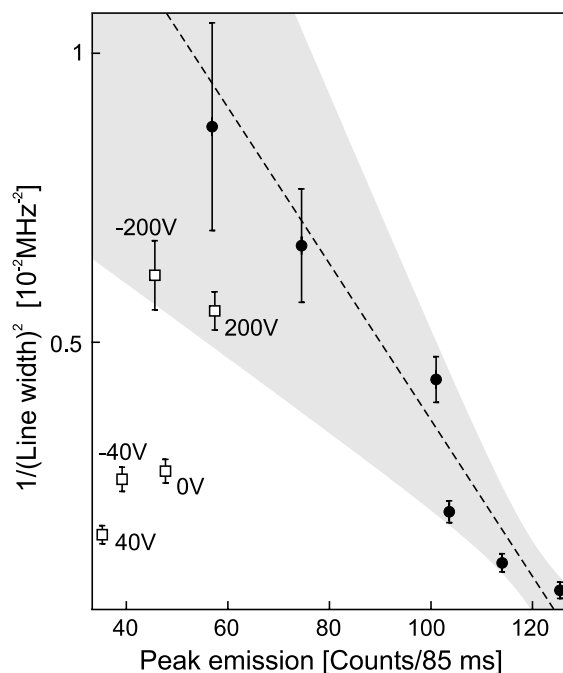


Fig. 4. Saturation study: $1/\Gamma^2$ plotted against the peak emission count rate R for molecule M1. Circles: Saturation data for the unperturbed molecule (tip retracted). Dashed line: linear fit. Shaded area: 95% confidence area obtained from the fit. Open squares: Selected data from the tip-induced Stark experiment labeled by the respective tip voltages.

(open squares). Only data points within the shaded area are compatible with unperturbed molecules. The two data points at large negative and positive voltages, where the TLSs are frozen, are within the shaded area. On the contrary, data taken from the plateau region of the Stark experiment are far outside the confidence area. This shows that the TLSs responsible for the spectral dynamics are actually induced or activated by the tip.

In conclusion, we have demonstrated that electric fields can be used to manipulate SM spectral dynamics that is activated by a tip. Further experiments are required to get more insights into the nature of these effects. Technical developments in combination with scanning probe methods will allow for a new class of SM experiments that provide accurate control of stress, electric field, and possibly also of charges injected by the tip.

Acknowledgements

The technical assistance of A. Hunkeler and B. Lambillotte is acknowledged. We thank B. Sick for preparing the tips and E. Donley, A. Kramer and R. Purchase for helpful discussions. This project was funded by the Swiss Priority Program NFP 36 and the ETH Zürich.

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