Enhanced control of single-molecule emission frequency and spectral diffusion

Supplemental Information

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Supporting Information Available

The Stark effect in DBT molecules

We consider here the effect of an external electric field $\vec{E}_\text{ext}$ on the spectral properties of a DBT molecule. In particular we focus on the so-called zero phonon line (ZPL), which here is given by the lowest electronic transition between the ground state $|0\rangle$ and the first excited state $|1\rangle$. By means of perturbation theory we obtain a shift of the $0 \to 1$ transition frequency in the form of

$$\Delta\omega = \vec{d} \cdot \vec{E}_\text{ext} - E_\text{ext}^i \alpha_{ij} E_\text{ext}^j. \tag{1}$$

Here the dipole moment is defined as $\vec{d} = e(\langle 1|\vec{r}|1\rangle - \langle 0|\vec{r}|0\rangle)$ and it gives the first order of the perturbation theory. For symmetry reason we can safely set it to zero $\vec{d} \approx 0$. The second order part instead is given by the polarizability tensor, formally wirtten as

$$\alpha_{ij} = \frac{e^2}{2} \left[\sum_{n\neq 1} \frac{\langle 1|r_i|n\rangle\langle n|r_j|1\rangle}{\hbar\omega_n - \hbar\omega_1} - \sum_{n\neq 0} \frac{\langle 0|r_i|n\rangle\langle n|r_j|0\rangle}{\hbar\omega_n - \hbar\omega_0} \right] \tag{2}$$

where $|n\rangle$ are the electronic eigenstates of the molecule. In this treatment we neglect the phoninc contributions, which are much out of resonance and they thus bring an almost zero contribution.

Considering the DBT main axis we have that the polarizability tensor is diagonal, completely determined by the $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$ components. Anyway, computing the polarizability tensor can be extremely challenging, since it requires to solve the full many-body electronic structure of the molecule.

Fortunately we can still obtain useful information by truncating that expression to the first three level (we notice that two levels are not enough, since the resulting polarizability would be always negative, in contrast with current observations). For each component we need to consider the first three levels for which the dipole matrix element are non-zero. For

the xx component we can infer this information from a previous work where the electronic structure and main optical properties are explicitly computed.[1] We then arrive to

$$\alpha_{xx} \approx \frac{e^2}{2} \left[\frac{\langle 1|x|2\rangle\langle 2|x|1\rangle}{\hbar\omega_2 - \hbar\omega_1} - 2\frac{\langle 0|x|1\rangle\langle 1|x|0\rangle}{\hbar\omega_1 - \hbar\omega_0} \right]. \tag{3}$$

With this expression we can now estimate the polarizability tensor.

The ZPL frequency of the DBT gives $\hbar\omega_1 - \hbar\omega_0 \approx 1.6\text{eV}$, while we can estimate $\hbar\omega_2 - \hbar\omega_1 \approx 2\text{eV}$, identifying it as a two-photon transition.[1] The matrix element $\langle 1|x|0\rangle$ can be obtained from the DBT ZPL dipole transition, which is typically assumed around $e\langle 1|x|0\rangle \sim 12\text{D}$.[1] The matrix element of the $1 \to 2$ transition is not known, but we can guess it. For a harmonic oscillator we would have $\langle 2|x|1\rangle = \sqrt{2}\langle 1|x|0\rangle$, for which the polarizability is exactly zero. So we expect that this matrix element can be assumed larger than this, reasonably still on the same order, giving an estimate $e\langle 2|x|1\rangle \sim 20 - 30\text{D}$. Putting everything together we can estimate the following range for the DBT polarizability

$$\frac{\alpha_{xx}}{\hbar} \approx 2\pi \times 0.2 - 2 \text{ MHz}/(\text{kV/cm})^2, \tag{4}$$

which is in agreement with previous estimations.[2]

Regarding the z-direction polarizability, we can guess to be non zero, but smaller than the x-direction one, $\alpha_{zz} < \alpha_{xx}$. This can be deduced again by considering the electronic eigenstates structure described.[1]

Effect of field charge on the excitation spectrum

The excitation spectrum, observed on time scale comparable or longer than the SD characteristic time, will be described by the convolution of the Fourier-limited DBT Lorentzian line centered at frequency ω, $L(\omega, \gamma_0)$, with the distribution probability associated to the

fluctuating frequency shift $p(\delta\omega)$ describing SD

$$S(\omega) = \int_{-\infty}^{+\infty} p(\delta\omega)L(\omega - \delta\omega, \gamma_0)d\delta\omega. \tag{5}$$

In general, there might be several other mechanisms responsible for spectral diffusion in quantum emitters, resulting in a central frequency which is randomly distributed, with a standard deviation σ, that is strongly dependent on the observation time. These are typically described in terms of interaction with a bath of two-level systems that can generate different broadening regimes depending on the coupling of the emitter to the bath and to the time scales involved in the process. Different regimes correspond to different $p(\delta\omega)$ following lorentzian, gaussian or Levy statistics for the most common cases.[3,4] A Gaussian broadening is used to analyze the measurements in this paper. This kind of broadening matches rigorously results obtained from the model when the fluctuation of the electric field are small enough that the paraboloid of Fig. **??**(c) of the main text can be locally approximated with a plane.

Stark effect and spectral diffusion after an optical shift

Here we report some other examples measured on other molecules in our sample. In Fig. 1(a) we show another observation of the Stark effect on several molecules after the whole sample was treated with the optical shift technique.[5] The effect of the optical shift here is to homogeneously shift all the molecules and turn to be mostly irrelevant for the spectral diffusion properties. As explained in the main text this is due to the fact that the optical shift represents a Stark effect along the z-axis of the molecule, giving a much smaller contribution to the SD.

From the highlighted parabola in Fig.1(a) we estimate the DBT polarizability $\alpha_{xx}/\hbar \approx 2\pi \times 1.65\text{MHz}/(\text{kV/cm})^2$, still consistent with what presented in the main text.

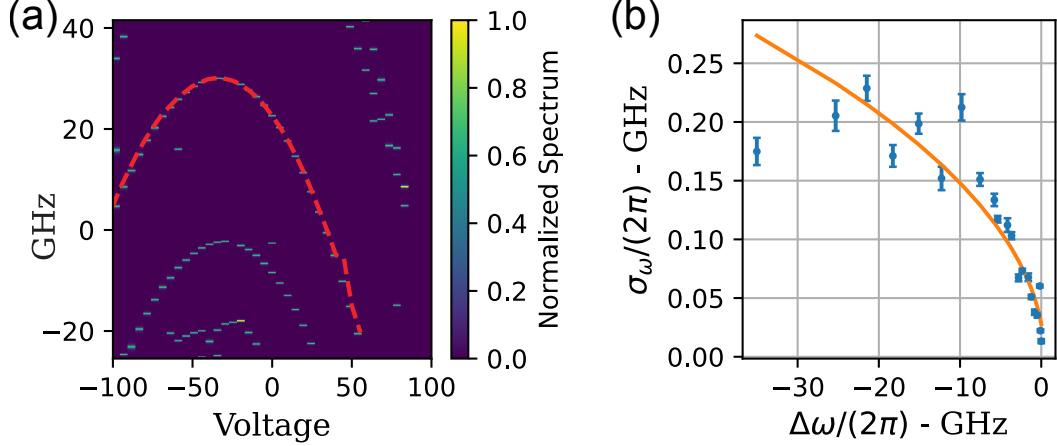As in the main text, the excitation spectrum is fitted with a Voigt profile fixing the

Figure 1: (a) The map of excitation spectrum $S(\omega)$ as a function of the applied voltage on the electrodes. This measurement is averaged over a time $\bar{t} \approx 2$s. (c) Measured spectral diffusion as a function of the frequency shift extracted from the data highlighted by the red dashed line in (a). The values of σ_ω are extracted by fitting each fixed voltage spectrum with a Voigt profile.

Lorentzian component on the Fourier limit $\gamma_{\text{lim}}/(2\pi) \approx 80$MHz. The extracted value for σ_ω is purely due to SD. σ_ω is fitted as a function of the measured Stark shift $\Delta\omega_{\text{ZPL}}$ using Eq. (**??**), as is shown in Fig. 1(b), obtaining $\alpha_{xx}\sigma_E^2/\hbar = 2\pi \times 0.53 \pm 0.01$ MHz. Using the estimated polarizability we have that the local electric field variance is $\sigma_E = 1.56 \pm 0.20$ kV/cm. This value is again compatible with what reported in the main text, and, at this average measure time $\bar{t} \sim 2$s, there is no evidence of a sensible contribution to the SD by the optical shift.

Long term SD time traces

We here report the time traces obtained for the SD measures whose integrated versions are in Fig.**??** of the main text.

Measured SD induced broadening can strongly depend on the time of observation. Data reported in Fig.**??**(c) and in Fig.1(c) can be used to validate our model and to extract estimates of the orders of magnitude of relevant quantities like σ_E. However while those measurements were performed over short periods of time (2 s for each point), we monitored SD fluctuations over much longer times having in mind the time scales of experiments similar
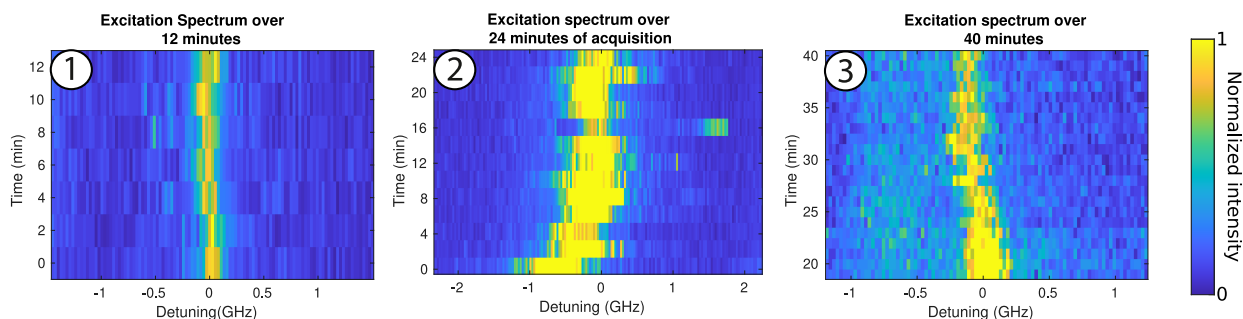
Figure 2

to those previously performed in our group.[6,7] In particular measurements 1, 2 and 3 have been integrated over 12, 24 and 42 minutes respectively.

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