The spin-Dicke effect in OLED magnetoresistance

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1. The spin-Dicke effect in resonantly driven weakly coupled spin-pairs

1.1 Collectivity induced by the spin-Dicke effect and the optical-Dicke effect

In this work, as throughout the literature, the term “Dicke effect” is used in the context of ensemble phenomena for which a collective ensemble state emerges which consists of mutually coherent excitations. For the Dicke effect which is studied here, collectivity is generated through the limit of very strong resonant excitation of nominally non-identical ensemble constituents (i.e. spin-$\frac{1}{2}$ transitions which are inhomogeneously broadened, predominantly by hyperfine fields). When the excitation field is sufficiently strong to ensure that the physical differences between these non-identical ensemble constituents have negligible influence on the ensemble when compared to the overall influence of the resonant driving field, the ensemble constituents assume an identical (i.e. phase coherent) state: the Dicke effect is established.

Both the optical Dicke effect, which has been studied extensively over the past six decades [1,2], as well as the spin-Dicke effect that is the focus of the present report, involve the generation of electromagnetic (EM) waves due to resonantly driven transition dipoles – electric dipoles for the optical-Dicke effect, magnetic dipoles for the spin-Dicke effect. Due to collective ensemble behavior, the amplitudes of these
EM waves increase proportionally to the ensemble size $N$. Thus, an $N^2$-dependence of the emitted power occurs, an effect referred to in the literature as “superradiance” [1]. For the optical Dicke effect, which usually involves electronic two-level transitions with both non-degenerate and degenerate eigenstates, destructive interference between the light components of degenerate transitions can lead to a quenching of superradiance, commonly referred to as “subradiance” [2]. For the spin-Dicke effect, however, neither superradiance nor subradiance plays a role. Subradiance does not arise when the driven spin system is described by a non-degenerate two-level system, which is the case for a Zeeman-split spin $s=\frac{1}{2}$ system or a weakly coupled (i.e. non-exchange coupled) pair of two such spins. Superradiance will exist for such a system but it will be undetectable in the EM field since the emergence of a collective spin-state requires resonant driving-field amplitudes $B_1$ of order of the static magnetic field $B_0$ which induces the two non-degenerate Zeeman sublevels. Since the only experimentally feasible way to establish this situation is to lower $B_0$ rather than raising $B_1$, spin polarization is negligible and the resonant radiation field (due to magnetic dipole transitions) is therefore vanishingly small.

The absence of subradiance or detectable superradiance in the presence of the spin-Dicke effect implies that conventional experimental approaches for its detection – e.g. by direct optical detection of superradiance – cannot be used. This limitation, however, does not mean that the spin-Dicke effect is not present in the system. Spin-dependent transport and recombination in organic semiconductors offer fundamentally alternative routes to observe collective spin effects without direct detection of radiation, as recently proposed by Roundy and Raikh [3].

### 1.2 Roundy-Raikh predictions regarding spin-dependent pair transition rates due to the onset of the spin-Dicke effect

Roundy and Raikh [3] give an analytical treatment of a conventional spin-$\frac{1}{2}$ pair triplet-singlet system undergoing magnetic resonance within the framework of organic magnetoresistance. In particular, they include the effect of spin-dependent singlet-pair recombination to predict the lifetime of the eigenstates of the system under different $ac$-drive strengths, and from this formulation they estimate the qualitative change in current from steady-state operation in different resonant driving regimes.

A non-trivial behavior of this change in current is predicted at high $ac$-drive strength, where the singlet recombination channel is isolated from the long-lived (three) triplet channels: while the triplet density throughout the spin-pair ensemble increases, leading to a quenching of the luminescent (radiative) singlet recombination rate, the device current, which is governed by spin-dependent pair recombination, increases.

This underlying behavior of the ensemble of spin $s=\frac{1}{2}$ pair constituents under resonant $ac$ drive is completely analogous to the Dicke effect for two-level systems. The sole difference lies in the manifestation of the effect through recombination-rate quenching rather than directly through the radiation field. We detect this recombination-rate quenching through the device current (it could also be measured through electroluminescence, but this is experimentally more challenging and brings no further insight). This detection approach is fundamentally different to conventional manifestations of the optical-Dicke effect in superradiance.
Note that the spin-Dicke effect-induced quenching of singlet recombination (fluorescence) is referred to by Roundy and Raikh as “subradiance”, an unconventional use of terminology. The physical manifestation of this spin-Dicke “subradiance” is fundamentally different to conventional subradiance of the optical-Dicke effect, since spin-dependent bright-dark transitions are considered. For the spin-Dicke effect, Roundy and Raikh refer to “subradiance” as a quenching of the spontaneous recombination rate, which is, of course, incoherent radiation. This terminology is in contrast to the coherent light emission caused by the optical Dicke effect. While this ambiguity in terminology may be confusing, the physical nature of the spin-Dicke effect in terms of a collective ensemble state involving mutually coherently propagating quantum states is nevertheless entirely analogous to the optical Dicke effect. Spin-collectivity is established by application of a resonant driving field strong enough to overcome the differences of the electron spins’ Larmor frequencies. These differences are caused by the randomly distributed local hyperfine fields and the random distribution of spin-orbit coupling (the Landé-factors).

When the spin-Dicke effect of weakly coupled pairs of spins with \( s = \frac{1}{2} \) evolves under the low-\( B_0 \) room-temperature conditions, the absence of spin-polarization in the ensemble implies that four collective subensembles of spin pairs evolve with mutually different spin-pair states (see Fig. 2 of Ref. [3]). While there is therefore no collective behavior between the constituents of these four subensembles, each of these macroscopic subensembles separately does undergo collective behavior.

### 1.3 Experimental verification of the spin-Dicke effect by testing the Roundy-Raikh predictions

The theoretical study by Roundy and Raikh [3] predicts that the spin-Dicke effect can emerge in ensembles of weakly coupled pairs of spins with \( s = \frac{1}{2} \) when all spin pairs couple phase-coherently to the driving field. In this case, dissociation and recombination transitions, which depend on spin-permutation symmetry, control the carrier-pair lifetime and therefore the current. The change in pair transition rate as a function of amplitude of a linearly polarized \( B_1 \) field (the driving field) and a perpendicularly oriented \( B_0 \) field (the detuning field) exhibits a characteristic behavior that displays the following features which differ substantially from resonant absorption effects conventionally detected by \( \text{cw} \) ESR absorption spectroscopy:

(i) a linear initial increase of the transition rate change (a linear decrease in current for the case where the relevant transition is charge-carrier recombination) with the driving field amplitude \( B_1 \); we note that experimentally the initial increase of the transition rate with \( B_1 \) actually follows a quadratic dependence when \( B_1 \) is below the power broadening regime \([ (\gamma B_1)^{-1} > \text{lifetime of the pairs}] \). This trivial very-low \( B_1 \)-regime is not discussed by Roundy and Raikh [3], though, and we therefore do not show measured data in this \( B_1 \) regime. The fit of the initial linear decrease of the normalized current in Fig. 2d) reveals slopes of \( \alpha_H = -2.47(13)/\text{mT} \) for the hydrogenated sample and \( \alpha_D = -4.25(22)/\text{mT} \) for the deuterated sample.

(ii) the existence of a transition rate saturation maximum at a specific \( B_1 \) field, determined by the detuning and the hyperfine fields (i.e. a minimum of the
(iii) a quadratic transition rate increase with $B_1$ when $B_0$ is sufficiently detuned (i.e. beyond the amplitude of the hyperfine field) from the resonance condition;

(iv) a linear transition rate change decrease with $B_1$ when $B_1$ is larger than the saturation maximum prior to the onset of the collective regime. The fit of this rate decrease (or increase when the rate is recombination) is predicted by theory to be smaller than the magnitude of the slope of the initial increase. Experimentally, the normalized current in Fig. 2d) reveals slopes of $\beta_H = -0.48(2)/\text{mT}$ for the hydrogenated sample and $\beta_D = -0.83(3)/\text{mT}$ for the deuterated sample, i.e. significantly smaller than the $\alpha$ slopes in point (i).

(v) a characteristic sign change of the spin-dependent transition rate when $B_1$ exceeds the threshold where collective effects become dominant; and, most importantly,

(vi) a universal scaling of this entire $B_1$ dependence with $B_{hyp}$, making it material independent. On two mutually scaled axes, the data for the normalized current change of the deuterated and hydrogenated samples indeed show excellent agreement when a scaling factor of $f=1.72(4)$ is applied to the scale of $B_1$ (see Fig. 1). This factor is consistent with the ratio of the expectation values of the hyperfine fields experienced by the paramagnetic centres in the two isotopically distinct MEH-PPV samples. These values can easily be obtained from the full width at half maximum of the magnetoresistance-measured line-shape (see discussion of this in section 2 below).

In the main text, the experimental verification of the predicted $B_1$ dependencies of transition rates (i) through (vi) as well as their dependence on the hyperfine fields, controlled by the isotope used, confirms the presence of the spin-Dicke effect without the need for measuring coherent radiation (with its quadratic driving-power and ensemble-size dependence) for the confirmation of superradiance. As noted above, it is not possible to measure radiative transitions for an ensemble of spin $s=\frac{1}{2}$ systems in the low-$B_0$ regime. This low-field regime is, however, crucial to reaching the parameter region necessary ($B_1 \approx B_0$) to reach the spin-Dicke regime.

2. The steady-state magnetic resonance line shape in magnetoresistance

As discussed in detail previously [4], electrically detected magnetic resonance spectra of MEH-PPV OLEDs exhibit a universal shape which is described by two Gaussian functions. One Gaussian arises from the hyperfine-field-broadened resonance of the positive charge carrier; the other Gaussian describes the resonance of the negative carrier. We demonstrate in Figure S1 that an $RF$ field change of the $dc$ magnetoresistance of both materials is well described by the sum of two Gaussian functions. Since electron and hole wave functions differ in $\pi$-conjugated materials, the
The double-Gaussian fit results of the data in Fig. S1 reveal good agreement with the experimental data with coefficients of determination of 0.99784 (for hydrogenated MEH-PPV, green line) and 0.99327 (for deuterated MEH-PPV, blue line). We note that the fit for the deuterium sample is not as good as for the protium sample for two reasons: first, since only the 2-ethylhexyloxy side groups of the MEH-PPV are deuterated, the distribution of hyperfine fields is still influenced by a small hydrogen ensemble which makes the overall distribution and hence the line shape more complex. Second, in contrast to the hydrogenated sample whose hyperfine distributions are broad, the narrow distribution in the deuterium device (with standard deviation $\sigma = 0.197$ mT) is only larger than the driving field $B_1 = 0.0714$ mT by a factor of about 2.75, and thus the distortion of the line width by power broadening is non-negligible. The power broadening effect could be suppressed by a choice of smaller $B_1$, however, as shown by Fig. 2, the observed current changes decrease linearly with $B_1$ in this $B_1$ regime and the vanishing signal also diminishes the fit accuracy.

**Figure S1:** Change of the magnetoresistance in response to the application of an RF field at 85MHz. The data are taken from Fig. 1d) and e). Fits for the two materials with double Gaussian functions reveal good agreement.

The resonance line shapes displayed in Fig. S1 represent the distribution of random hyperfine fields experienced by charge carriers which contribute to the measured device current. From these distributions, we estimate the ratio of the overall expectation values for the hyperfine field strength $B_{\text{hyp}}$ of the hydrogenated and deuterated samples, respectively, from the ratio of the full widths at half maximum (FWHM), following the procedure employed by Nguyen et al. [5]. We find FWHM$_H = 0.96(3)$ mT and FWHM$_D = 0.51(3)$ mT, and thus $B_{\text{hyp}}^H/B_{\text{hyp}}^D = 1.88(13)$. Within the error range, this is in agreement with the scaling factor of $f = 1.72(4)$ of the $B_1$ scale in Fig. 2. This agreement demonstrates that the dependence of the magnetoresistance change is universal and scaled by $B_{\text{hyp}}$ only, just as described by Roundy and Raikh [3]. We note that the factor $f \approx B_{\text{hyp}}^H/B_{\text{hyp}}^D$ is smaller than the ratio of nuclear magnetic moments of the proton and the deuteron $\mu_p/\mu_d = 2.79285 \mu_N/0.8574\mu_N = 3.2572$ (with $\mu_N$ the nuclear magneton). This difference is expected since $B_{\text{hyp}}$ in the deuterated material is determined by hyperfine fields of both protons and deuterons located at various distances relative to the electron and hole polaron wave functions.
3. Determination of the RF field strength

In order to calibrate the amplitude $B_1$ of the RF field, the frequency of magnetic resonance induced spin-Rabi oscillation (i.e. precession of spin states about the RF field under magnetic resonance) was measured. As this experiment was conducted on the paramagnetic states that control the sample current, the spin-Rabi oscillation could be detected by current measurements. The frequency of the electrically detected spin-Rabi oscillation was then converted to the magnitude of the driving field by using the known gyromagnetic ratio [6] of the polymer’s charge carrier states (for MEH-PPV, $\gamma = 28.03(4)$ GHz/T).

![Graphs showing current change and field strength vs. pulse length](image)

**Figure S2:** a) Plot of the device current change at 26.8μs after the device was irradiated with a short RF pulse as a function of the applied pulse length. The current reveals spin-Rabi oscillations. b) Plot of the spin-Rabi oscillation frequency $\Omega_R$ as a function of the square root of the applied power $P$. The data reveal agreement with the expected linear dependence.
The $B_1$ calibration followed our previously reported electrical detection of spin-Rabi oscillation at high $B_0$ fields [4]: the oscillating field was applied as a short pulse under magnetic resonant conditions ($B_0 = 3.1$mT, with an RF frequency of 85MHz), and the device current change in response to this pulse at a time $t_0 = 26.8\mu$s after the end of the pulse was determined as a function of the applied pulse length. The result of this series of measurements is displayed in Fig. S2a) for various applied RF powers. Each data set reveals an oscillatory dependence of the measured current change, which is due to the control of the current by coherent spin motion of the charge carrier spins. Each data set is displayed along with the result of its fit by an exponentially decaying sine function. The data were obtained for pulse lengths ranging from 60ns (the lower cutoff of the Pulseblaster pulse generator) to about 900ns in steps of 14ns (the minimal interval of the Pulseblaster). Figure S2a) reveals the expected increase of the oscillation frequency with power for the RF powers for which the experiment was performed. Figure S2b) displays a plot of the Rabi-frequencies $\Omega_R$ obtained from the fits of the data in Fig. S2a) as a function of the square root of the applied RF power. As expected for spin-Rabi oscillation for which $B_1 = 2\pi \Omega_R/\gamma$, the dependence of $\Omega_R$ on $\sqrt{P}$ shows excellent agreement with a linear function through the origin. From the linear fit of the power dependence displayed in Fig. S2b), one can extrapolate the relationship between the RF power and $B_1$ for any arbitrary RF power.

4. Error analysis

The current measurement for each combination of $B_0$ and $B_1$ was repeated 20 times. Each run was recorded separately so as to obtain an accurate measurement of the fluctuations in the current at each field. By determining the current on resonance for each individual run, we found the standard deviation of the sample current through the estimator for an unbiased sample variance. The error of $B_1$ was determined from the error of the square-root-of-power to $B_1$ conversion factor that was obtained from the linear fit of the data in Figure S2b).

References