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Phys. Rev. B 85, 245437 — Published 20 June 2012
DOI: 10.1103/PhysRevB.85.245437
Isotope effect in the spin response of aluminum tris(8-hydroxyquinoline) based devices

Tho D. Nguyen¹, T. P. Basel¹, Y-J. Pu², X-G. Li³, E. Ehrenfreund¹,⁴ and Z.V. Vardeny¹*

¹Department of Physics & Astronomy, University of Utah, Salt Lake City, UT 84112, USA
²Department of Organic Device Engineering, Yamagata University, Yonezawa, 992-8510 Japan
³Hefei National Laboratory for Physical Sciences at Microscale, Department of Physics, University of Science and Technology of China, Hefei 230026, PRC
⁴Department of Physics, Technion-Israel Institute of Technology, Haifa 32000, Israel

Abstract

We studied the spin response of various magnetic field effects and magneto-transport in both protonated and deuterated aluminum tris(8-hydroxyquinoline) [Alq₃]-based organic light emitting diodes and spin-valve devices. Both conductivity-detected magnetic resonance in diodes and magneto-resistance in spin valves show substantial isotope dependence pointing to the importance of the hyperfine interaction (HFI) in the spin response of spin ½ charge polarons in Alq₃. In addition the low field (B<20 mT) magneto-electroluminescence (MEL) response is also isotope sensitive, showing that HFI-induced spin mixing of polaron-pairs spin sublevels dominates this response too. However, the magneto-conductance (MC) response was found to be much less sensitive to isotope exchange at low fields, in agreement with previous studies. The disparity between the isotope sensitivity of MC and MEL responses in Alq₃ indicates that the HFI in the MC response is overwhelmed by an isotope independent spin mixing mechanism. We propose that collisions of spin ½ carriers - with triplet species such as polaron pairs may be the main spin mixing mechanism in the low field MC response in Alq₃ diodes.

* To whom correspondence should be addressed; e-mail: val@physics.utah.edu
I. INTRODUCTION

Aluminum tris(8-hydroxyquinoline) (Alq₃) [see molecular structure in Fig. 1(a) inset] is a common active molecular layer used in organic light emitting devices (OLED), due to its efficient electro-luminescence (EL) emission and high electron mobility 1-3. It is thus not surprising that magnetic field effects (MFE) in Alq₃-based OLED devices such as magneto-electroluminescence (MEL) and magneto-conductance (MC) have been extensively studied in the last few years 4-10. As a result, several basic models were originally proposed to explain the obtained magnetic-field effect response, MFE(B). Basically, all models agree that the underlying mechanism for the MFE is the magnetic field dependence of spin sublevel mixing; but there is no consensus as to the basic excitation species in which the spin-mixing occurs. The competing models include: (i) spin mixing in oppositely charged polaron-pairs (PP) and in pairs of same-charge polarons (or bipolarons, BP) by the hyperfine interaction (HFI)⁴,⁶,¹¹,¹²; (ii) spin mixing within triplet-triplet annihilation (TTA) process ⁷; and (iii) spin mixing during the process of triplet exciton quenching by spin ½ charge polarons ⁸. Importantly, the HFI proposed models should differ substantially from the other models in the response to isotope exchange in the Alq₃ molecule active layer, where all hydrogen atoms (nuclear spin I_H=½, nuclear g-factor g_H=5.586) are exchanged by deuterium atoms (I_D=1, g_D/g_H=0.154). This should occur since the HFI constant, a_HF, scales with the nuclear g-factor ¹³, whereas the other proposed interactions are mostly isotope insensitive. Consequently, the isotope exchange effect on the MFE(B) response in Alq₃-based OLED was recently studied to scrutinize the proposed spin-mixing models ⁹,¹⁴. It was concluded that the MFE in Alq₃-based OLED is not dominated by PP or BP species, since it was found that the HFI does not play a major role in determining the MC(B) and MEL(B) responses. This conclusion is surprising because similar MFE measurements in devices based on a common π-conjugated polymer, namely poly(dioctyloxy) phenyl vinylene (DOO-PPV), have shown a substantial isotope effect ¹⁵,¹⁶. It is thus important to investigate in more detail the influence of the isotope exchange on the MFE and magneto-transport in Alq₃ based devices, in order to identify the underlying spin-exchange mechanisms.

In this work we present a detailed study of the MFE response and magneto-transport in protonated (H⁻) and deuterated (D⁻) Alq₃-based OLED and spin-related devices. These studies include spin ½ conductivity detected magnetic resonance (CDMR) in organic diodes, magneto-
resistance (MR$_{SV}$) in organic spin valves (OSV), and MC and MEL responses in OLED devices. We found that the spin ½ CDMR is isotope sensitive. It shows a narrower resonant line in D-Alq$_3$ compared to H-Alq$_3$ devices, and therefore the polaron excitation in Alq$_3$ is definitely influenced by the HFI. This indicates that spin-related effects based on polaron excitations should be isotope sensitive in this molecule. Indeed we measured superior MR$_{SV}$ response in D-Alq$_3$ OSV devices, which indicates larger spin diffusion length due to the reduced HFI with the deuterium isotope nuclei. Moreover a clear sizable isotope dependent MEL($B$) response in OLED was also observed at low fields ($B$<~20 mT), showing that HFI-induced spin mixing of polaron-pairs spin sublevels plays a crucial role also in determining the MEL response in Alq$_3$-based OLED. However the MC($B$) response at low fields was found to be much less sensitive to the isotope exchange. In addition at high fields both MEL($B$) and MC($B$) responses are isotope insensitive, and do not show the expected HFI-related saturation up to $B$~250 mT. These puzzling MFE characteristic properties can be understood taking into consideration that in addition to the HFI in PP (or BP) species, other spin-mixing mechanisms also participate in determining the MFE in Alq$_3$ diodes. We propose that an isotope independent collisions of spin ½ polarons with spin triplet species (e.g. PP, BP or TE) is the main spin mixing mechanism responsible for the low field MC($B$) response.

II. EXPERIMENTAL

The active layers in our spin-related device studies were the following two Alq$_3$ isotopes: H$_{18}$Alq$_3$ and D$_{18}$Alq$_3$, where all the hydrogen atoms in H-Alq$_3$ were replaced by deuterium $^{17}$. Figures 1(a) and 1(b) (left insets) show the Alq$_3$ molecular structure and the H (D) atoms positions. We used both NMR spectroscopy and infrared (IR) absorption to verify that all hydrogen atoms were replaced by deuterium atoms in the D-Alq$_3$ molecules. The IR absorption spectrum of the two Alq$_3$ isotopes in the range of the C-H stretching vibration, $\nu_{CH}$, shows a deuteration related shift according to the expected mass ratio (Fig. 1(a), right inset). We measured $\nu_{CH}$=3050 cm$^{-1}$ and $\nu_{DH}$=2276 cm$^{-1}$; and thus their ratio is within 2% of the square root C-D/C-H reduced mass ratio. In particular the lack of an absorption band at 3050 cm$^{-1}$ in the IR absorption spectrum of D-Alq$_3$ indicates that there are little or no hydrogen atoms present in this molecule.
The Alq₃-based OLED devices were fabricated using glass substrates coated with 40 nm of indium-tin-oxide (ITO) that were purchased from Delta Technologies. The conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT) [H C Starck] was spin-coated onto the ITO used as the anode. The H-Alq₃ (D-Alq₃) that was synthesized in house was then thermally evaporated onto the bottom electrode. Subsequently a Ca cathode with an Al capping layer was deposited by thermal evaporation onto of the Alq₃ thin film. The complete device structure configuration was ITO/PEDOT(30nm)/Alq₃(70nm)/Ca(20nm)/Al(50nm) having an active area of ~2x2 mm².

For the CDMR measurements the Alq₃-based OLED devices were placed in an S-band (~3 GHz) microwave (MW) cavity in a cryostat at 10K equipped with MW throughput cables; the MW radiation was provided by a Gunn diode that delivered up to Pₖₑₚ ~0.1 W power. The cryostat was placed inside a liquid He cooled superconducting coil that provided magnetic fields up to 3 Tesla, applied perpendicular to the device substrate. Pₖₑₚ was modulated at frequency f~200 Hz and the change, ΔI, in the current I was monitored using a lock-in amplifier at f. The magnetic field B was swept while monitoring ΔI. Resonance condition for spin ½ and g≈2 occurs when the MW photon energy is equal to the energy difference between the two Zeeman split spin sublevels at B~0.1 T. For comparing the resonance profile of the two Alq₃ isotopes we measured ΔI(B)/I under identical conditions such as device structure, applied voltage, temperature and microwave power.

For the MEL and MC measurements, the Alq₃-based OLED devices were transferred to an optical cryostat with variable temperature that was placed in between the two pole pieces of an electromagnet that produced B in the range ±0.3 T with 10⁻⁵ T resolution; in all measurements B was determined by a calibrated magnetometer. The devices were driven at constant voltage V or constant current I using a Keithley 236 apparatus; whereas the EL intensity was measured by a Si photo-detector, while sweeping B in both positive and negative directions. The MC(B) (MEL(B)) is defined by the relation ΔI(B)/I(0) [ΔEL(B)/EL(0)], and is positively defined when I increases with B.

The OSV devices were fabricated using the half-metal La₀.₆₇Sr₀.₃₃MnO₃ (LSMO) as the spin injector FM anode. The Alq₃, Co and Al layers were successively thermally evaporated onto the
LSMO electrode, similar to the OLED fabrication described above. The OSV device structure was LSMO(200nm)/Alq₃(40nm)/Co(6nm)/Al(50nm) with an active area typically of ~0.2x0.4 mm². All thermal evaporations were done in a high vacuum environment (5x10⁻⁷ mbar). The film thickness was measured using thickness profilometry (KLA Tencor). The OSV magneto-resistance response, MRₜ, was measured in a closed-cycle refrigerator at temperatures, T, in the range 10-300 K using the ‘four probe’ method in a constant current mode using a Keithley 236 apparatus, while varying the external in-plane magnetic field. The magnetization properties of the FM electrodes were measured by the magneto-optic Kerr effect (MOKE); from these measurements we determined typical low temperature (10 K) coercive fields of the unassembled electrodes as B₁~4.5 mT and B₂~15 mT for the LSMO and Co electrodes, respectively.

III. RESULTS AND ANALYSIS

A. Conductivity detected magnetic resonance

The CDMR spectra of H- and D-Alq₃ OLED devices (Figs. 1(a) and 1(b), respectively) is negative under magnetic resonance conditions. CDMR in π-conjugated systems measures changes in the polaron pair (PP) density under resonance conditions. Therefore the CDMR spectra in Fig. 1 show the effect of isotope exchange on the PP spin density. The resonance line of H-Alq₃ is inhomogeneously broadened; the full width at half maximum (FWHM) is ~3.94 mT for the H-Alq₃ and 3.54 mT for the D-Alq₃, substantially larger than the FWHM (<2 mT) obtained in spin ½ CDMR of devices based on DOO-PPV polymer. Using the same model presented earlier in Ref.16, we show fits (black solid lines in Fig. 1) to the measured CDMR line shapes of the H- and D-Alq₃ devices using an inhomogeneously broadened hyperfine split resonance line with αHF=3 mT and 0.46 mT, respectively. The smaller FWHM measured for the D-Alq₃ device is a strong indication that the HFI indeed plays an important role in the PP spin dynamics in this molecule.

B. Magneto-resistance in organic spin-valves

Further evidence for the HFI importance for spin ½ polarons in Alq₃ is revealed in the magneto-resistance (MRₜ) measurements in OSV devices based on D- and H-Alq₃ interlayer (Fig. 2). It
is seen that MR_{SV} of D-Alq_3 (Fig. 2b) is three times larger than that of H-Alq_3 (Fig. 2a). The superior MR response of the D-Alq_3 OSV is maintained at various voltages (Fig. 2c), showing that the spin diffusion length, \( \lambda_s \), in the deuterated spin valve is substantially larger than that in the hydrogenated device. \( \lambda_s \) in OSV devices increases with the spin relaxation time, \( \tau_s \): (a) for carrier diffusion motion, \( \lambda_s = \sqrt{D\tau_s} \), where \( D \) is the carrier diffusion constant which is proportional to the carrier mobility, \( \mu \), via the Einstein relation; (b) For carrier drift motion in an applied electric field \( F \), \( \lambda_s = \mu F \tau_s \). Assuming that carrier mobility is not influenced by the isotope exchange, we conjecture that the larger \( \lambda_s \) obtained in D-Alq_3 OSV is due to longer spin \( \frac{1}{2} \) relaxation time; and this also points to the importance of the HFI in the spin \( \frac{1}{2} \) polaron transport in Alq_3 devices.

C. Magneto-electroluminescence in OLEDs

C.1 The low field regime

The MEL(\( B \)) response of H- and D-Alq_3 OLED are shown with various field resolution in Figs. 3(a)-(c); a clear isotope dependent response can be seen. First, the width \( \Delta B \) of the MEL(\( B \)) response in H-Alq_3 device is \( \sim 40\% \) larger than that in D-Alq_3 (Fig. 3(b) and Fig. 3(a) inset). This observation is at variance with an earlier study in which much smaller dependence on the isotope exchange was reported \(^9,14\). Second, the MEL(\( B \)) response shows another feature at low fields (\( B < \sim 2 \) mT) [Fig. 3(c)]: as \( |B| \) is varied from \( B=0 \) MEL(\( B \)) is negative, reaches a minimum value at \( |B|=B_m \), then monotonically increases thereafter, including a zero crossing. We clearly see that \( B_m \) is isotope dependent: \( B_m=0.2 \) mT for D-Alq_3 and 0.4 mT for H-Alq_3. Similar features, dubbed ultra-small magnetic field effect (USMFE) were previously obtained in DOO-PPV based OLEDs, where the isotope dependence was shown to originate from the HFI in PP species \(^15,16\). We therefore conclude that the HFI in PP species plays a dominant role also in the low-field MEL response in Alq_3 devices. We note however, that the obtained ratios \( B_m(H)/B_m(D) \approx 2 \) and \( \Delta B(H)/\Delta B(D) \approx 1.4 \) in Alq_3 OLEDs are about 30-40\% smaller than those measured in DOO-PPV isotopes \(^16\). This observation indicates that in addition to the HFI, other interactions that are isotope insensitive have to be taken into account for explaining the detailed MEL response in Alq_3 \(^14\). An in-depth discussion of the isotope effect in the low field MEL Alq_3 response is presented in sections IV and V below.
C.2 The high field regime

At higher fields ($|B|\approx 50-250$ mT) the MEL response does not level off; instead it continues to increase, in contrast to what is expected for MFE response governed by the HFI\textsuperscript{11,16}. This characteristic behavior indicates that a different mechanism is dominant for the high field response of both MEL and MC. Alq\textsubscript{3} is known to have phosphorescence emission from triplet excitons (TE) and delayed fluorescence caused by triplet-triplet-annihilation\textsuperscript{19}. Therefore it is likely that TE are involved in the MFE response at intermediate high fields, via high order recombination. In order to examine this hypothesis we exposed the Alq\textsubscript{3} based OLED devices to oxygen atmosphere, which is known to quench TE species\textsuperscript{20}. Figure 4 shows the MEL($B$) response of oxygen-exposed OLED devices of both Alq\textsubscript{3} isotopes. The MEL response is similar to that shown in Fig. 3, but with much clearer difference between the responses of the two isotopes. The MEL width of H-Alq\textsubscript{3} OLED defined in Fig. 4, is now twice larger than that of D-Alq\textsubscript{3} OLED. This shows that the intermediate high field MEL response obtained in unexposed devices comes from TE, which is insensitive to isotope exchange. When this component is quenched by exposure to oxygen then the HFI-dominated component prevails, and consequently the isotope dependent response becomes clearer.

D. Magneto-conductance in OLEDs

Figures 3(d)-(f) show the MC($B$) response measured on the same OLED devices in which the MEL($B$) responses were measured (Figs. 3(a)-(c)). Although the MC($B$) responses seem to be similar to MEL($B$), the isotope dependence is different. Figure 3(f) shows that at low fields $B_{m}(H)\approx B_{m}(D) (\approx 0.6$ mT) for the MC response, whereas the ratio $B_{m}(H)/B_{m}(D)\approx 2$ for the MEL response. Also when the isotope dependent MC responses are normalized at the maximum measured field of $B_{max}\approx 220$ mT (Fig. 3(e)), then the two responses appear to be much less isotope sensitive than the MEL responses (Fig. 3(a)). This indicates that a mechanism \textit{other than the HFI} dominates the MC($B$) response at low fields ($|B|<20-30$ mT).

IV. DISCUSSION

A. The polaron-pair mechanism: isotope sensitive MEL response

As argued in section III the low field MEL($B$) response should be described by the PP mechanism, with the HFI as the main spin mixing process. Since the measured MEL($B$) response
shows significant isotope effect, the spin orbit coupling and/or the exchange interaction contributions are relatively small here. For completeness we now present the PP mechanism model which is based on the time evolution of the PP spin sublevels in a magnetic field, and is closely related to the well-known "radical-pair" mechanism \(^{21,22}\); versions of this model were described in more details previously \(^{16,23}\). We note that the MEL\((B)\) response isotope dependence can be also explained by the BP model \(^{11}\).

The basic PP spin Hamiltonian, \(H_0\), includes the Zeeman, HFI and exchange terms:

\[
H_0 = H_{\text{Zeeman}} + H_{\text{HF}} + H_{\text{ex}}
\]  

In Eq. (1) \(H_{\text{HF}}\) is the HFI term,

\[
H_{\text{HF}} = \sum_{i=1}^{2} \sum_{j=1}^{N_i} a_{ij} \vec{S} \cdot \vec{I}_{ij},
\]

where \(a_{ij}\) is the isotropic HFI describing the interaction between polaron spin \(S_i\) (\(=\frac{1}{2}\)) and \(N_i\) neighboring nuclei, each with spin \(I_{ij}\). For protons in organic molecules the HFI constant is of the order of \(a\(H\)=0.3 \, \mu\text{eV} \) (or \(a/g\mu_B\approx 3 \, \text{mT}\)) \(^{13}\). The electronic Zeeman interaction term in Eq.(1) is

\[
H_{\text{Zeeman}} = \mu_B \left( g_1 \vec{S}_1 + g_2 \vec{S}_2 \right) \cdot \vec{B}
\]

where \(g_i\) (\(\approx 2\)) is the respective g-factor of each of the polarons in the PP species, and \(\mu_B\) is the Bohr magneton. Finally the exchange interaction is written as

\[
H_{\text{ex}} = 2\mu_B B_{\text{ex}} \vec{S}_1 \cdot \vec{S}_2,
\]

where \(B_{\text{ex}}\) measures the strength of the exchange interaction (we chose here for simplicity scalar HFI, g-factors and exchange interaction). In the absence of the spin orbit interaction the configuration space of \(H_0\) is of dimension \(M = 4 \prod_{i=1}^{2} \prod_{j=1}^{N_i} (2I_{ij} + 1)\). We did not specifically include the spin orbit interaction in Eq. (1), but it could in principle be calculated for the Alq3 molecule.
When the MEL (and/or MC) response originates from spin mixing within the PP species, then it is controlled by the relative PP singlet and triplet fractions, and their spin dependent decay processes such as fusion into excitons or dissociation into free charges. These decay processes are not contained in the spin Hamiltonian, Eq. (1) as $H_0$ is an Hermitian operator that conserves energy. A convenient way to include the spin dependent decay kinetics is to add to $H_0$ a non-Hermitian decay (relaxation) term $^{22,24}$:

$$H_R = -\frac{i\hbar}{2} \sum_{\alpha} \gamma_{\alpha} P_{\alpha}$$

(5)

where $\alpha$ designates the 4 singlet and triplet states: namely $\alpha = S, T_0, T_{\pm 1}$; and $P_{\alpha}$ and $\gamma_{\alpha}$ are the state projection operator and decay rate constant, respectively. The time evolution of the decaying density operator is now expressed in terms of the total Hamiltonian, $H=H_0+H_R$,

$$\sigma(t) = \exp(-iHt/\hbar)\sigma^0 \exp(iH^t_{\dagger}t/\hbar)$$

(6)

where $H^\dagger$ is the Hermitian conjugate of $H$, and the $t=0$ density matrix $\sigma^0$ is determined by the PP generation process. The time evolution of the singlet and triplet PP fraction may now be written as,

$$\rho_{\alpha}(t) = \text{Tr}(P_{\alpha}\sigma(t)) = \frac{4}{M} \sum_{n,m} P_{n,m}^{\alpha}\sigma^0_{nm} \cos(\omega_{nm} t) \exp(-\gamma_{nm} t)$$

(7)

where $E_n = \hbar(\omega_n - i\gamma_n)$ are the (complex) eigen-values of $H$, $\omega_{nm} = \omega_n - \omega_m$; $\gamma_{nm} = \gamma_n + \gamma_m$ the double summation $(n,m)$ is over all M states. Equation (7) expresses the fact that the PP singlet (or triplet) time evolution contains both a coherent character (through the $\cos(\omega_{nm} t)$ factor) and an exponential decay factor. The measured MFE (that is MC and MEL) may directly be calculated using Eq. (7). The final expression for the MEL response depends on the radiative recombination of the SE and the detailed relaxation route from PP to form SE. We denote the effective SE generation rate from the PP$^{\alpha}$ configuration by $k_{\alpha,SE}$. Consequently, we define the “SE generation yield”, $\Phi_{SE} = \sum_{\alpha} \Phi_{\alpha,SE}$, where $\Phi_{\alpha,SE}$ is given by

$$\Phi_{\alpha,SE} = \int_0^\infty k_{\alpha,SE} \rho_{\alpha}(t) dt = \frac{4}{M} \sum_{n,m} P_{n,m}^{\alpha}\sigma^0_{nm}(0) \frac{k_{\alpha,SE}\gamma_{nm}}{\gamma_{nm}^2 + \omega_{nm}^2}$$

(8)
The contribution of the PP mechanism to the \( MEL(B) \) response is then given by
\[
MEL_{pp}(B) = \frac{\Phi_{SE}(B) - \Phi_{SE}(0)}{\Phi_{SE}(0)}. \tag{9}
\]

In Figs. 5(a) and 5(b) we show the simulated \( MEL_{pp} \) response, using Eq. (9) for two HFI cases
(i) H-Alq3 with \( I=\frac{1}{2} \) and \( a_{HF}/g\mu_B=4 \) mT; and (ii) D- Alq3 with \( I=1 \) and \( a_{HF}/g\mu_B=0.6 \) mT. In both cases the exchange and SOC strengths were chosen to be \( \sim0.2 \) mT. Comparing the simulation to the MEL data presented in Figures 3(b) and 3(c) we conclude that the isotope dependent width and USMFE minima are captured by the PP mechanism with the HFI as the main spin mixing process.

B. Collision of spin ½ polaron with triplet-state polaron-pair: low field MC response

Unlike the MEL response discussed above, the obtained \( MC(B) \) response does not show much isotope effect due to HFI, indicating the dominance of a different spin mixing mechanism. In this section we introduce a novel, isotope insensitive mechanism that affects the MC response but does not affect the MEL response. That the MEL and MC responses are not similar to each other in Alq3 was recently measured and discussed \(^25\).

The many PP that are produced from the injected free carriers do not have a fixed inter-polaron distance, \( d_P \), but rather form a distribution of \( d_P \)'s. As the PP fuse to form excitons, \( d_P \) gradually decreases while the singlet and triplet states PP, namely \( PP_S \) and \( PP_T \), separate in energy until the appropriate values for the SE and TE in the material are reached. In the intermediate state, where spin mixing between \( PP_S \) and \( PP_T \) is already diminished due to their large energy separation, \( PP_T \) still evolves with \( B \) because of its non-zero spin. Also \( PP_T \) may interact with spin ½ carriers via magnetic spin-spin interaction. Such an interaction may be described by a ‘collision process’ in which a spin ½ carrier (“polaron”) is temporarily paired with a close \( PP_T \) neighbor which causes magnetic field dependent carrier density that forms a finite \( MC(B) \) response. This mechanism does not contribute to MEL, and is insensitive to isotope exchange. The contribution to \( MC(B) \) comes from the direct \( PP_T \) dissociation, thus leading to isotope independent MC response. Similar triplet-doublet interaction has been considered before in connection with TE quenching by free radicals \(^26\), as well as for mobilization of trapped charge carriers in molecular crystals \(^27\).
Similar to the triplet-doublet collision model \(^{26}\), we envision the carrier-PP collision event as a process by which the \(S_1=1\) \(PP_T\) and \(S_2=\frac{1}{2}\) charge carrier are temporarily paired together (forming a \(PP_T-P\) pair), which evolves with time in a magnetic field, and then dissociates into free carrier and \(PP_T\), respectively. The \(PP_T-P\) species may be either in a quartet (\(S=S_1+S_2=3/2\)) or doublet (\(S=S_1-S_2=\frac{1}{2}\)) spin states. The \(PP_T-P\) species spin Hamiltonian in a magnetic field may be written as

\[
H_p = H_{ppt} + J_p \vec{S}_1 \cdot \vec{S}_2 + H_Z + H_R
\]

(10)

where \(H_Z\) is the Zeeman energy term given by Eq. (3) with \(g_1, g_2\) as the \(PP_T\) (free carrier) \(g\)-factor, \(J_p\) is the \(PP_T-P\) spin-spin interaction constant, and \(H_{ppt}\) is the \(PP_T\) triplet spin Hamiltonian term given by

\[
H_{ppt} = \vec{S}_1 \cdot \vec{\tau} \cdot \vec{S}_1
\]

(11)

where \(S_1=1\) is the \(PP_T\) spin and \(\vec{\tau}\) is the triplet \(^{28}\) symmetric traceless tensor of rank 2. In the triplet principal reference frame:

\[
H_{ppt} = D_P (S_{1_z}^2 - 2/3) + E_P (S_{ix}^2 - S_{iy}^2),
\]

where \(D_P\) and \(E_P\) are referred to as the \(PP_T\) zero field splitting (ZFS) parameters. The decay of the quartet and doublet states (with decay constants \(\gamma_Q\) and \(\gamma_D\), respectively) is represented by the non-Hermitian relaxation term \(^{22,24}\) \(H_R\) in Eq. (10), similar to Eq. (5). Following the procedure outlined in section IV.A above we may now calculate the magnetic field dependent density of free polarons that dissociate out of the \(PP_T-P\) pairs. Denoting the dissociation rate from the \((PP_T-P)^\alpha\) (\(\alpha=\text{quartet, doublet}\)) configuration by \(d_\alpha\), the free polaron yield and its contribution to MC are given by Eqs. (8)-(9), with \(d_\alpha\) in place of \(k_{\alpha,SE}\). The decay and dissociation constants (\(\gamma_\alpha\) and \(d_\alpha\)) determine mainly the magnitude of the MFE, whereas the triplet parameters \(D_P\) and \(E_P\) determine the overall width and the behavior at low fields (for \(E_P<<D_P\), respectively. In Fig. 5(b) we show a simulated MC(\(B\)) response for \(D_P/g\mu_B=50\) mT and \(E_P/g\mu_B=0.45\) mT. The simulated response is isotope insensitive, and features the sign change and minimum at \(B<1\) mT as in the experiment (Fig. 3(f)). It is important to note that in addition to this proposed mechanism, other triplet based mechanisms (e.g. polaron collision with TE) exist in the literature, and may be also responsible for the high field MFE response.
V. SUMMARY

Using the spin ½ CDMR and MRsv in OSV devices based on H- and D-Alq3 we showed that the HFI is indeed a significant spin relaxation mechanism for spin ½ polarons in Alq3. Moreover, the HFI provides an important spin mixing mechanism for polaron-pairs in Alq3 that may explain the MEL(B) response. The reduced HFI in D-Alq3 with respect to H-Alq3 is clearly observed in a variety of spin ½ related experiments. We obtained: (a) narrower spin ½ CDMR resonance line in D-Alq3; (b) longer spin diffusion length in OSV based on D-Alq3; (c) narrower MEL(B) response and smaller Bm in OLEDs based on D-Alq3. In contrast, the MC(B) response is much less sensitive to isotope exchange and thus the HFI-based spin mixing mechanism here is overwhelmed by another, isotope insensitive spin mixing mechanism. To explain the low field behavior of MC in Alq3 we offer an isotope independent interaction between free carrier with S=½ and triplet-state PP.

Acknowledgments

This work was supported in part by the NSF (Grant # DMR-1104495 and MRSEC program (DMR-1121252) at the UoU; T.D.N and Z.V.V.); the Israel Science Foundation (ISF 472/11; E.E.), and the US-Israel BSF (Grant # 2010135; Z.V.V. and E.E.).
References

FIG. 1. (Color online) Spin $\frac{1}{2}$ CDMR of (a) H$_{18}$-Alq$_3$ (red line) and (b) D$_{18}$-Alq$_3$ (blue line) measured at ~3 GHz and 10 K; the FWHM are 3.94 and 3.46 mT, respectively. The black lines are fits using inhomogeneous broadened (Gaussian profile, FWHM=3.4 mT) hyperfine split resonance, with $a_{HF}$=3 mT and 0.46 mT, respectively, for H-Alq$_3$ and D-Alq$_3$. The molecules’ chemical structures are shown in the left insets. The right inset in (a) shows the molecules’ infra-red absorption spectra (red for H-Alq$_3$ and blue for D-Alq$_3$), having a red-shifted C-D stretching mode that occurs upon deuteration; namely $\nu_{CH}=3050$ cm$^{-1}$ and $\nu_{DH}=2276$ cm$^{-1}$. 
FIG. 2. (Color online) The spin valve related magnetoresistance, $\text{MR}_{\text{SV}}(B)$ response of two 40 nm thick OSV devices based on (a) H-Alq$_3$ and (b) D-Alq$_3$, for up (black) and down (colored) $B$-sweeps, measured at $V=12$ mV and $T=10$ K. (c) Bias voltage dependence of $|\text{MR}_{\text{SV}}|_{\text{max}}$ for H-Alq$_3$ (red squares) and D-Alq$_3$ (blue circles).
FIG. 3. (Color online) (a)-(c) MEL(\(B\)) response of OLEDs based on H-Alq\(_3\) (red line) and D-Alq\(_3\) (blue line) measured at room temperature and bias \(V=4V\), plotted at three different \(B\) scales. The D-Alq\(_3\) response was normalized to that of H-Alq\(_3\) at \(B\sim250\) mT. Inset in (a): The full width, \(\Delta B\), measured at MEL=0.8% plotted vs. \(V\) for H-Alq\(_3\) (red) and D-Alq\(_3\) (blue). (d)-(f) Same as in (a)-(c) but for the MC(\(B\)) responses measured on the same devices.
FIG. 4. (Color online) MEL(B) response of OLEDs based on H- and D-Alq3 saturate-exposed to oxygen, measured at $V=4\text{V}$ and room temperature. The full width, $\Delta B$, measured at MEL=1\% is 12.4 mT (6.6 mT) for the H-Alq3 (D-Alq3) device. The response of D-Alq3 was normalized to that of H-Alq3 at $B=200$ mT.
FIG. 5. (Color online) Model simulation for the low field MEL and MC responses of Alq3. (a) PP mechanism for MEL($B$) of H- and D-Alq3: red line, $a/g\mu_B=2.5$ mT, $I=1/2$ (H); blue line, $a/g\mu_B=0.4$ mT, $I=1$ (D). A finite exchange interaction of strength $B_{ex}=0.02$ mT was used for both responses. (b) Polaron/PP$T$ scattering model for the isotope independent MC($B$). The line shown was calculated using the zero-splitting parameters $D_{p}/g\mu_B=50$ mT and $E_{p}/g\mu_B=0.45$ mT in the triplet spin Hamiltonian.