Transverse spin relaxation time in organic molecules: A possible platform for fault tolerant room temperature quantum computing

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Abstract

We report measurement of the ensemble averaged transverse spin relaxation time ($T_2^*$) in bulk and few molecules of the organic semiconductor tris(8−hydroxyquinolinolato aluminum) or Alq$_3$. This system exhibits two characteristic $T_2^*$ times, the longer of which is temperature-independent and the shorter is temperature-dependent, indicating that the latter is most likely limited by spin-phonon interaction. Based on the measured data, we infer that the single particle $T_2$ time is long enough to meet Knill’s criterion for fault tolerant quantum computing, even at room temperature. Alq$_3$ is also an optically active organic and we propose a simple optical scheme for spin qubit read out. Moreover, we found that the temperature-dependent $T_2^*$ time is considerably shorter in bulk Alq$_3$ powder than in few molecules confined in 1-2 nm sized cavities, which is suggestive of a new type of “phonon bottleneck effect”. This is very intriguing for organic molecules where carriers are always localized over individual molecules but the phonons are delocalized.

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The $\pi$-conjugated organic semiconductor Alq$_3$ exhibits exceptionally long longitudinal spin relaxation time $T_1$ (approaching 1 second at 100 K) because of weak spin-orbit interactions \[1\]. That bodes well for classical spin based devices like Spin Enhanced Organic Light Emitting Diodes \[2\] or classical spin based computing paradigms such as Single Spin Logic \[3, 4\] where a long $T_1$ time reduces the probability of bit errors caused by unwanted spin flips. In quantum computing paradigms \[5, 6, 7, 8, 9, 10\], the bit error probability depends on the transverse spin relaxation time $T_2$ rather than $T_1$. The probability of a spin based qubit to decohere during a qubit operation that lasts for a time duration $T$ is roughly $1 - e^{-\frac{T}{T_2}}$. Knill has shown that fault tolerant quantum computing becomes possible if this probability is less than 3% \[11\], i.e., if $T_2/T > 33$.

Two recent results have inspired us to look towards the Alq$_3$ molecule as a potential candidate for fault-tolerant spin based quantum computing. The first is the demonstration that it exhibits a long $T_1$ time \[1\]. This results from weak spin orbit interactions which could also make the $T_2$ time long enough to allow fault tolerant computing. Second, some organic molecules can be efficient quantum processors with high gate fidelity \[12\]. These two factors, taken together, raise the hope that Alq$_3$ might be a preferred platform for spin based quantum computing. This molecule also has spin-sensitive optical transitions that can be gainfully employed for spin (qubit) read out. That makes it even more attractive.

Unfortunately, it is very difficult to measure the single particle $T_2$ time directly in any system (including Alq$_3$ molecules) since it requires complicated spin echo sequences. Therefore, we have measured the ensemble averaged $T_2^*$ time instead, since it can be ascertained easily from the line width of electron spin resonance spectrum. This time however is orders of magnitude shorter than the actual $T_2$ time of an isolated spin because of additional decoherence caused by interactions between multiple spins in an ensemble \[13, 14\]. It is particularly true of organics where spin-spin interaction is considered to be the major mechanism for spin decoherence \[15\]. Consequently, bulk samples (where numerous spins interact with each other) should behave differently from one or few molecules containing fewer interacting spins. In the rest of the paper, we will designate the $T_2^*$ times of bulk and few-molecule samples as $T_{2b}^*$ and $T_{2f}^*$, respectively. We have found that they are discernibly different.

In order to prepare samples containing one or few molecules, we followed the approach in ref. \[16\]. We first produced a porous alumina film with 10-nm pores by anodizing an aluminum foil in 15% sulfuric acid \[17\]. A two-step anodizing process was employed to
improve the regimentation of the pores [18]. These porous films were then soaked in 1, 2-dichloroethane (C₂H₄Cl₂) solution of Alq₃ for over 24 hours to impregnate the pores with Alq₃ molecules. The films were subsequently washed several times in pure C₂H₄Cl₂ to remove excess Alq₃. There are cracks of size 1-2 nm in the anodic alumina film produced in sulfuric acid [16, 19, 20]. Ref. [16] claims that when the anodic alumina film is soaked in Alq₃ solution, Alq₃ molecules of 0.8 nm size diffuse into the cracks and come to rest in nanovoids nestled within the cracks. Since the cracks are 1-2 nm wide, only 1-2 molecules of Alq₃ can reside in the nanovoids. Surplus molecules, not in the nanovoids, will be removed by repeated rinsing in C₂H₄Cl₂ [16]. C₂H₄Cl₂ completely dissolves out all the Alq₃ molecules, except those in the nanovoids, because the C₂H₄Cl₂ molecule cannot easily diffuse through the 1-2 nm wide nanocracks to reach the nanovoids. Therefore, after the repeated rinsing procedure is complete, we are left with an ensemble of few-molecule clusters in the nanovoids. The nanovoids are sufficiently far from each other that interaction between them is negligible [16]. Therefore, if we use the fabrication technique of ref. [16], we will be confining one or two isolated molecules in nanovoids and measuring their T₂⁺ times. In contrast, the T₂⁻ times are measured in bulk Alq₃ powder containing a very large number of interacting molecules.

The T₂⁺ and T₂⁻ times were measured using electron spin resonance (ESR) spectroscopy. In each run, 20 samples of area 25 mm² each were stacked. They together contain 5 × 10¹¹ pores and even if each pore contains at least one molecule and each molecule contains at least one electron (extremely conservative estimate), we still have over 5 × 10¹¹ electrons, which are more than adequate to provide a strong spin signal (our equipment can measure signals from 10⁹ spins).

It is well known that Alq₃ has two spin resonances corresponding to Landé g-factors of approximately 2 and 4 [21]. Ref. [21] determined from the temperature dependence of the ESR intensity that the g = 4 resonance is associated with localized spins in Alq₃ (perhaps attached to an impurity or defect site) while the g = 2 resonance is associated with quasi free (delocalized) spins. From the measured line widths of these two resonances, we can estimate the T₂⁺ and T₂⁻ times for each resonance individually using the standard formula

\[
T_2^f \text{ or } T_2^b = \frac{1}{r_e (g/2) \sqrt{3\Delta B_{pp}}}
\]

where \( r_e \) is a constant = 1.76 × 10⁷(G – s)⁻¹, \( g \) is the Landé g-factor and \( \Delta B_{pp} \) is the full-width-at-half-maximum of the ESR line shape (the line width). We checked that the line
shape is almost strictly Lorentzian, so that the above formula can be applied with confidence [22]. Fig. 1 shows a typical magnetic field derivative of the ESR spectrum obtained at a temperature of 10 K corresponding to \( g = 2 \) resonance. There are three curves in this figure corresponding to the blank alumina host, bulk \( Alq_3 \) powder, and \( Alq_3 \) in 1-2 nm voids. The alumina host has an ESR peak at \( g = 2 \) (possibly due to oxygen vacancies) [23], but it is much weaker than the resonance signals from \( Alq_3 \) and hence can be easily separated. Note that the g-factor of the isolated \( Alq_3 \) molecules in nanovoids is slightly larger than that of bulk powder since the resonance occurs at a slightly higher magnetic field. More importantly, the bulk powder has a broader line width than the few molecules confined in the nanovoids. This is a manifestation of the fact that stronger spin-spin interactions in the bulk powder reduce the effective \( T_2^* \) time, i.e., \( T_2^b < T_2^f \).

In Fig. 2, we plot the measured \( T_2^f \) and \( T_2^b \) times (associated with the resonance corresponding to \( g = 2 \)) as functions of temperature from 4.2 K to 300 K. The inequality \( T_2^b < T_2^f \) is always satisfied except at one anomalous data point at 4.2 K. There are two important points to note here. First, both \( T_2^f \) and \( T_2^b \) are relatively temperature independent over the entire range from 4.2 K to 300 K. This indicates that spin-phonon interactions do not play a significant role in spin dephasing. Second, both \( T_2^f \) and \( T_2^b \) times are quite long, longer than 3 nanoseconds, even at room temperature.

In Fig. 3, we plot the measured \( T_2^f \) and \( T_2^b \) times as functions of temperature corresponding to the \( g = 4 \) resonance. The \( T_2^f \) time is plotted from 4.2 K to 300 K, but the \( T_2^b \) time in bulk powder can only be plotted up to a temperature of 100 K. Beyond that, the intensity of the ESR signal fades below the detection limit of our equipment. The features to note here are that: (1) \( T_2^f \) and \( T_2^b \) are no longer temperature independent unlike in the case of the \( g = 2 \) resonance. \( T_2^f \) decreases monotonically with increasing temperature and falls by a factor of 1.7 between 4.2 K and 300 K, (2) \( T_2^b < T_2^f \) and the ratio \( T_2^f / T_2^b \) decreases with increasing temperature. The maximum value of the ratio \( T_2^f / T_2^b \) is 2.4, occurring at the lowest measurement temperature of 4.2 K, and (3) both \( T_2^f \) and \( T_2^b \) times are about an order of magnitude shorter for the \( g = 4 \) resonance compared to the \( g = 2 \) resonance.

The strong temperature dependence of \( T_2^f \) and \( T_2^b \) tells us that for \( g = 4 \) resonance, spin-phonon coupling plays the dominant role in spin dephasing instead of spin-spin interaction. The spin-phonon coupling is absent or significantly suppressed for the \( g = 2 \) resonance, which is why \( T_2^f \) and \( T_2^b \) are an order of magnitude longer and also temperature independent for \( g \).
= 2. Ref. [21] has ascribed the $g = 2$ resonance to quasi free carrier spins in $Alq_3$ (whose wavefunctions are extended over an entire molecule) and $g = 4$ resonance to localized spins (whose wavefunctions are localized over an impurity atom). If that is the case, then it is likely that the localized spins and the delocalized spins will have very different couplings to phonons since their wavefunctions are very different.

An interesting question is why should $T_2^f$ be so much longer than $T_2^b$ for the $g = 4$ resonance. The bulk has many more interacting spins than the few-molecule sample has, but if spin-spin interaction is overshadowed by spin-phonon coupling, then this should not make any difference. What could be causing this behavior is a new type of phonon-bottleneck effect. For $g = 4$ resonance, we know that the primary dephasing agents are phonons. So what makes the spin-phonon coupling so much stronger in bulk than in nanovoids? In bulk $Alq_3$ powder, the phonons are not confined and form a continuum. However, in isolated nanovoids (cavities) of $\sim 2$ nm diameter, the phonons are confined so that only discrete phonon modes are allowed. Any dephasing transition will then have to emit or absorb a subset of these allowed phonon modes. This reduces the transition probability considerably since few phonons are available to satisfy the energy and momentum conservations for phonon emission and absorption. This is a new type of phonon bottleneck effect, slightly different from the one discussed in ref. [26], which required carrier confinement more than phonon confinement. This new type of phonon bottleneck effect would explain why $T_2^f > T_2^b$ when phonons are the primary dephasing agents. The bottleneck will be more severe at lower temperatures since fewer phonon modes will be occupied (Bose Einstein statistics), which is exactly what we observe. If this explanation is true, it will be the first observation of this effect in organic molecules. What makes it more intriguing is the fact that there is no quantum confinement effect on electrons since their wavefunction is at best extended over a single molecule which is only $\sim 0.8$ nm in size, but the phonon modes are extended over many molecules and therefore do suffer quantum confinement if the confining space is a nanovoid of $\sim 2$ nm in diameter. We raise the specter of phonon bottleneck only as a possibility, but cannot confirm it experimentally beyond all reasonable doubt since that would require showing progressive suppression of dephasing with decreasing nanovoid size, something that is experimentally not accessible. Nonetheless, we believe that there is a strong suggestion for the phonon bottleneck effect.

We conclude by discussing the suitability of $Alq_3$ molecules for quantum computing ap-
plications. For a single isolated spin in $Alq_3$, $T_2$ should be at least an order of magnitude longer than $T_2^*$ \[13, 14\] particularly when spin-spin interaction is the major dephasing mechanism ($g = 2$). Since we have measured that $T_2^* \sim 3$ nanosecond at nearly all temperatures between 4.2 K and 300 K for $g = 2$ resonance, we expect that the single spin $T_2$ time will be at least 30 nanoseconds over this entire temperature range. Now, if Rabi oscillation is used for qubit operations such as rotation \[7, 8\], then the time taken to effect a complete spin flip is $T = h/(2g\mu_B B_{ac})$ where $g$ is the Landé g-factor, $\mu_B$ is the Bohr magneton and $B_{ac}$ is the amplitude of the ac magnetic field inducing the Rabi oscillation. With $B_{ac} = 500$ Gauss \[27\], $T = 0.35$ nanoseconds. Therefore, the error probability $= 1 - \exp[-T/T_2] = 1.15\%$. This is less than the Knill limit of 3\% for fault tolerant quantum computing, which is encouraging. We emphasize that $Alq_3$ does not have exceptionally long $T_2$ times, but it is still adequate for fault tolerant quantum computing. Nitrogen vacancy $NV^-$ in diamond exhibits a much longer $T_2$ time of several tens of $\mu$sec at room temperature \[28\]. However, quantum computing paradigms based on $NV^-$ require optical gating \[29, 30\] or cavity dark states \[31\] since it would be nearly impossible to place an electrical gate on top of an atomic vacancy using any of the known fabrication methods. As a result, $NV^-$ computers are not truly scalable. In contrast, the spins in $Alq_3$ are not bound to specific atomic sites. Instead, they extend over molecules of size $\sim 1$ nm, which allows electrical gating and therefore scalable renditions of quantum processors. Inorganic semiconductor qubit hosts, that will also allow electrical gating, typically have a shorter $T_2^*$ time than $Alq_3$ at room temperature \[32\]. Therefore, the $Alq_3$ system deserves due attention.

Finally, if an $Alq_3$ quantum dot were used as a host for a spin qubit, one would require a mechanism for reading the host spin (qubit read out). Fortunately, this can be achieved quite simply and elegantly. It is well known that only the singlet exciton recombines radiatively in $Alq_3$ and the triplet does not \[2\]. Thus, one needs to inject a spin polarized hole into an $Alq_3$ quantum dot that hosts a single electron in the LUMO level, from a p-type dilute magnetic semiconductor such as GaMnAs. The hole’s spin will be known (majority spin in GaMnAs). If a photon is emitted from the $Alq_3$ quantum dot, then we will know that the electron’s spin and the hole’s spin are anti-parallel. Otherwise, they are parallel. This allows one to determine the electron’s spin polarization in the $Alq_3$ dot (qubit read out). The optical read out mechanism requires a quantum dot photon detector to be integrated on top of the $Alq_3$ quantum dot hosting the spin. This is not difficult to implement \[33\] and does not detract
from the scalability. In conclusion, $Alq_3$ based quantum processors (1) are scalable, (2) are capable of fault-tolerant operation at room temperature, (3) possibly have a high degree of gate fidelity, and (4) lend themselves to an elegant qubit read out scheme. This makes them attractive candidates for quantum computers.

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FIG. 1: First derivative in magnetic field of the electron spin resonance spectrum corresponding to \( g = 2 \). The three curves are the data for the blank alumina matrix, the \( \text{Alq}_3 \) powder and \( \text{Alq}_3 \) molecules in nanovoids. The temperature is 10 K.

FIG. 2: Transverse spin relaxation times as a function of temperature for \( g = 2 \) resonance. The two plots are for bulk \( \text{Alq}_3 \) powder \( (T_2^p) \) and few \( \text{Alq}_3 \) molecules in nanovoids \( (T_2^f) \).
FIG. 3: Transverse spin relaxation times as a function of temperature for \( g = 4 \) resonance. The two plots are for bulk Alq\(_3\) powder (\( T_2^b \)) and few Alq\(_3\) molecules in nanovoids (\( T_2^f \)).