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Motional modes in bulk powder and few-molecule clusters of tris(8-hydroxyquinoline aluminum) and their relation to spin dephasing

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The ensemble averaged spin dephasing rate of localized electrons in the organic molecule tris(8-hydroxyquinoline aluminum) or Alq₃ has been found to be significantly larger in bulk powder than in single- or few-molecule clusters confined within 1–2 nm sized nanocavities [B. Kanchibotla *et al.*, Phys. Rev. B **78**, 193306 (2008)]. To understand this observation, we have compared the midinfrared absorption spectra of bulk powder and single- or few-molecule clusters. It appears that molecules have additional vibrational modes in bulk powder possibly due to multimerization. Their coupling with spin may be responsible for the increased spin dephasing rate in bulk powder. © 2011 American Institute of Physics. [doi:10.1063/1.3554753]

There is significant interest in understanding the dephasing mechanism of a single spin in an organic molecule^{1–5} since the latter can be an excellent host for spin-based qubits. Quantum gates fashioned out of spins in organic molecules possess remarkable gate fidelity⁶ and there exists a unique and elegant scheme for qubit readout that has no direct analog in inorganic systems.³

Recently, two interesting results were reported. The ensemble averaged spin dephasing time (T_2^*) of electrons bound to defect or impurity sites in the organic molecule tris(8-hydroxyquinoline aluminum) or Alq₃ (C₂₇H₁₈N₃O₃Al) was found to (1) be ~2.5 times shorter in bulk powder than in single- or few-molecule clusters confined in 1–2 nm sized nanocavities and (2) decrease rapidly with increasing temperature in the range of 4.2–100 K, indicating that dephasing is mediated by interaction with time-dependent perturbations such as phonons, molecular vibrations, etc.³

There are many possible reasons why T_2^* in bulk powder and in few-molecule clusters confined in nanocavities could be different. Kanchibotla *et al.*³ hypothesized that a nanocavity may confine environmental acoustic phonons and discretize their energies.⁷ In that case, spin-phonon interaction, which might be a major route for dephasing, will be suppressed in a nanocavity if phonons whose energies are resonant with spin splitting energies are not allowed within the cavity owing to the specific boundary conditions. One could think of this as a nontraditional phonon bottleneck effect, somewhat different from the traditional one.⁸ Such an effect will increase the spin dephasing time in a nanocavity. A second possibility is that the effect has nothing to do with the nanocavity but is entirely due to intermolecular interactions. Molecules in bulk powder can form multimers because of strong intermolecular interactions and experience enhanced electron-phonon interaction as a result.⁹ In one- or two-molecule clusters, they can only form monomers or dimers and the electron-phonon interaction is weaker.⁹ This will increase the spin dephasing time in single- or few-molecule clusters over that in bulk powders. A third possibility is that

formation of multimers in bulk powder could introduce additional rotational and vibrational modes in the molecules. Coupling of these additional modes with spins may increase the spin dephasing rate. This is actually not that different from the second possibility since the molecular vibrations and rotations can be viewed as “phonons.” The only difference is that instead of increasing the strength of electron-phonon coupling (the matrix element), this mechanism increases the number of available phonon modes, which also results in stronger electron-phonon interaction.

In order to investigate the third possibility, we prepared one- or two-molecule clusters of Alq₃ within 1–2 nm sized nanocavities. We then measured their midinfrared (mid-IR) absorption spectra in the wave number range of 2000–4000 cm⁻¹ (wavelength of 2.5–5 μm) and compared them to the absorption spectra of bulk powder. The infrared absorption spectrum of molecules is a signature of the vibrational and rotational modes. Our purpose was to see if the absorption spectra in this frequency range are different in bulk powder and in one- or two-molecule clusters since that would indicate a difference in the rotational and vibrational modes.

In order to fabricate 1–2 nm sized nanocavities that will host few-molecule clusters, we followed the method in Refs. 3 and 10. We first anodized a 99.999% pure aluminum foil of 0.1 mm thickness in 15% sulfuric acid at 10 V dc (at room temperature) for 15 min to produce an ~1 μm thick porous alumina film on the surface of the foil containing pores with diameter of 10 nm.¹¹ There are cracks with diameter of 1–2 nm in the pore walls^{10,12,13} that end in a small nanovoid of 1–2 nm diameter. Reference 3 contains a transmission electron micrograph of such a crack. Formation of these nanofissures and the nanovoids has been explored exhaustively by many groups in the past.^{10,12,13} The nanovoids act as the “nanocavities.” Because their linear dimensions are 1–2 nm and the Alq₃ molecule has a size of 0.8 nm, only one or two molecules can be accommodated within any nanovoid. Therefore, by trapping Alq₃ within these nanovoids and flushing them out from everywhere else, we can synthesize one- or two-molecule clusters.

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FIG. 1. (Color online) Room temperature photoluminescence spectrum of Alq_3 molecules trapped within 1–2 nm sized nanocavities in alumina. The peak at 497 nm is due to direct transition across the HOMO-LUMO gap, while the other peaks are either due to interference of waves reflected from front and back of the sample or due to impurities introduced during the processing steps.

Since we have to measure infrared absorption of the clusters, we need a substrate that is transparent to infrared. Unfortunately, metallic aluminum, on which the porous alumina film is formed, absorbs infrared radiation and is opaque. Therefore, the porous alumina film has to be released from the aluminum substrate before filling the nanocavities with Alq_3 . For this purpose, an organic varnish is brushed on the porous film and the sample is soaked overnight in HgCl_2 solution which selectively etches aluminum. The varnish provides mechanical stability to the film (which is only about 1 μm thick) during the release phase. The released sample is carefully inspected to ensure that no aluminum is present and then transferred to a beaker filled with ethanol to dissolve out the varnish. The ultrathin porous film floats to the surface of ethanol after the heavy varnish dissolves, and it is captured on a glass slide that is transparent to midinfrared.

The sample is then soaked in 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) solution of Alq_3 overnight to impregnate both the 1–2 nm cracks and the 10 nm pores with Alq_3 molecules. Huang *et al.*¹⁰ claimed that Alq_3 molecules of size 0.8 nm diffuse through the cracks and come to rest in the nanovoids where the cracks terminate. After many hours of soaking in the Alq_3 solution, the samples are withdrawn and then rinsed repeatedly in $\text{C}_2\text{H}_4\text{Cl}_2$ to remove any Alq_3 molecule from within the pores and everywhere else but leaving behind the molecules in the nanovoids since $\text{C}_2\text{H}_4\text{Cl}_2$ cannot diffuse through 1–2 nm cracks and wash out the molecule from within a nanovoid.¹⁰ The $\text{C}_2\text{H}_4\text{Cl}_2$ molecules evaporate quickly in air, leaving behind the one- or two-molecule clusters trapped in the nanovoids. This completes sample preparation.

It is not possible to ascertain with high resolution microscopy that the clusters are actually present in the nanovoids. Therefore, we carried out room-temperature photoluminescence (PL) measurements on these samples to confirm

(a)

(b)

FIG. 2. (Color online) Midinfrared absorption spectrum of (a) one- or two-molecule clusters of Alq_3 hosted in the nanocavities and (b) bulk powder of Alq_3 .

the presence of the clusters. Since Alq_3 is optically active, it luminesces in the wavelength range of 400–600 nm, unlike its host (porous alumina produced in sulfuric acid). This allows us to sense the presence of the clusters. The PL spectrum of porous films containing clusters is shown in Fig. 1. In each case, the PL of blank samples (containing no Alq_3) was subtracted from the PL of Alq_3 bearing samples in order to ascertain that the resulting PL is due to the Alq_3 clusters alone.

The PL spectrum has three peaks at 497, 516, and 536 nm, corresponding to photon energies of 2.48, 2.39, and 2.30 eV. There is also a broad shoulder at 480 nm. The peak at

497 nm is due to direct transition across the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of Alq_3 and was also observed in Refs. 9 and 10 which measured the PL spectrum of Alq_3 molecules trapped in porous alumina prepared in sulfuric acid. The broad shoulder and the other peaks could be due to interference of light reflected from the front and back of the porous alumina film or could be due to impurity states introduced during the unique processing steps. Since they have no bearing on the subject of this investigation, we did not probe them further. Overall, our PL is very similar to those in Refs. 9 and 10. This gives us confidence that the organic molecules are present in the nanovoids and have not been removed by rinsing in $\text{C}_2\text{H}_4\text{Cl}_2$. Transmission electron microscopy in Ref. 3 had ascertained that there are no Alq_3 clumps left outside the nanocavities either. Therefore, we can be reasonably certain that the only places occupied by the Alq_3 molecules are the nanocavities. Furthermore, because of the known size of the nanocavities, we can be confident that most clusters contain one or two molecules and not many more.

Finally, mid-IR absorption spectra of Alq_3 molecules confined within nanocavities were measured using Fourier transform infrared spectroscopy in a Nicolet spectrometer. Since a single sample did not produce enough absorption to be detected by our equipment with adequate signal-to-noise ratio, we had to stack three samples to measure absorption. In all cases, the absorption spectra were obtained by subtracting the spectrum of blank samples (that do not contain any organics but are otherwise nominally identical with organic bearing samples) from the latter. The spectrum was always averaged over a large number of scans to ensure that it was independent of the number of scans.

The absorption spectrum of Alq_3 clusters in nanocavities is shown in Fig. 2(a) in the wave number range of 2200–4000 cm^{-1} . For comparison, we have plotted the absorption of bulk Alq_3 powder in this range in Fig. 2(b). Note that the bulk powder's absorption increases monotonically with wave number, but the absorption of clusters is non-monotonic and shows a very broad peak centered at $\sim 3400 \text{ cm}^{-1}$. In this range, pure Alq_3 should have a peak at 3050 cm^{-1} due to stretching motion of the $\text{C}=\text{H}$ bond and another at 3400 cm^{-1} due to stretching motion of the hydroxyl bond.¹⁴ They may have merged to form the broad peak. Clearly, the absorption in clusters decreases rapidly at high wave numbers above 3600 cm^{-1} , but the absorption in bulk powder does not. The obvious conclusion is that motional modes that contribute to the high frequency absorption in powders are *absent* in the clusters. These additional modes that occur in powders but not in clusters are most likely due to creation of multimers which form when many molecules

are present within range of intermolecular interactions. Multimerization can obviously occur in bulk powders but cannot occur in clusters since they contain only one or two molecules.

The Alq_3 monomer has 52 atoms and 300 degrees of freedom for rotational and vibrational motions.¹⁵ Dimers and multimers have many more atoms than monomers and correspondingly more degrees of freedom giving rise to many more possible vibrational and rotational modes. Therefore, it is natural to find additional IR absorption in powders where multimers can form. It is noted that the additional modes crowd around the high frequency end of the IR spectrum, but its cause is not well understood. Nonetheless, the rotational and vibrational motions associated with these additional modes would couple to electron spin and could be responsible for the increased spin dephasing rate in powders.

In conclusion, we have shown that the previously reported increase in the spin dephasing rate in bulk powders of Alq_3 compared to one- or two-molecule clusters³ could be due to multimerization in the powder. This does not rule out other possible mechanisms for the increase but certainly establishes multimerization as one possible cause. This could be an important consideration for all of “organic spintronics” since organic molecules—unlike inorganic semiconductors—are susceptible to multimerization.

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