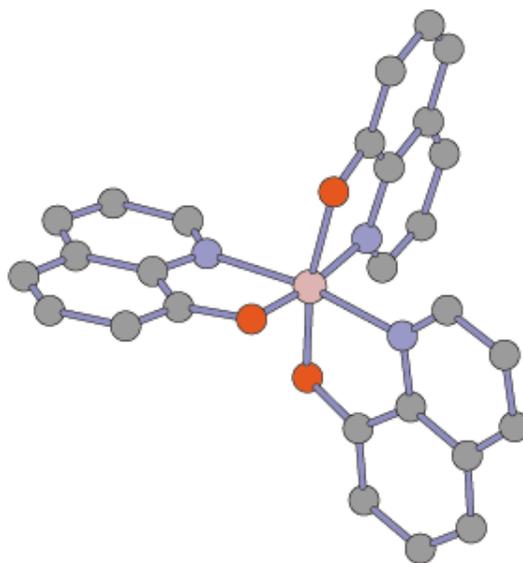


## Thin Film Properties of the Light-Emitting Diode Material Alq from Molecular Calculations

Richard L. Martin (T-12), Joel D. Kress (T-12), Ian H. Campbell (MST-11), and Darryl L. Smith (MST-11)

Conjugated organic materials are now used as the emissive layer in organic light-emitting diodes and they are also being investigated for a large variety of other electronic applications. It is of both scientific interest and technological importance to be able to predict the properties of dense solid state films based on the properties of the isolated, constituent organic molecules. It is particularly desirable to be able to predict the solid state electronic properties using calculated molecular properties since this would assist rational design of individual molecules for device applications. Our general goal is to be able to use calculated properties on the molecular scale to predict solid state film properties on the meso scale and then incorporate these solid state properties into a predictive device model on the macroscopic scale.

Two important organic electronic devices are light-emitting diodes and field effect transistors. For these devices critical solid-state properties include the solid-state ionization potential ( $IP_s$ ), the solid state electron affinity ( $EA_s$ ), the single particle energy gap ( $E_g = IP_s - EA_s$ ), and the charge carrier mobilities and optical properties near the absorption



**Figure 1: The meridional isomer of Alq. The central Al is coordinated by three oxygen atoms, two along the vertical axis and one in the equatorial plane, and three nitrogens in the equatorial plane.**

threshold. The single particle energy gap,  $IP_s$  and  $EA_s$  largely determine the charge injection properties of metal electrodes in contact with the organic material and the carrier mobilities determine the current in the device for a given charge density and electric field. The optical properties near the absorption threshold are important for light-emitting diodes.

Tris-(8-hydroxyquinolate)-aluminum, Alq (pictured in Figure 1), has been widely studied experimentally because of its use in light-emitting diodes [1]. Films of Alq are used as both light emitting and as electron transport layers. Although Alq

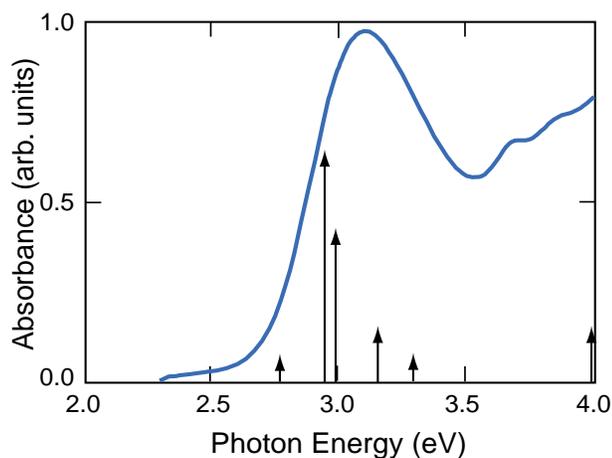
is typically used in multiple organic layer device structures, it has recently been studied in single layer structures where the properties of thin Alq films can be measured more directly [2].

**We discovered that the molecular calculations can describe the optical spectrum near the fundamental absorption threshold without significant corrections for solid-state effects.**

A number of important questions affecting device performance in Alq can be addressed with molecular calculations. For example, what is the magnitude of geometrical relaxation about the carriers (both hole and electron)? Are they similar? What is the resulting effect on mobility? Are there significant "excitonic" effects in the luminescence? To address

these questions we have performed molecular calculations using a hybrid density-functional-theory approximation known as B3LYP. The excited states were treated by time-dependent density-functional-theory with the same hybrid functional. We specifically considered: the optical spectrum near the fundamental absorption threshold, the energy, geometry, and characteristics of the lowest triplet state, the ionization potential and electron affinity, the single particle energy gap, the static dielectric constant and the electric field dependence of the electron mobility.

We discovered that the molecular calculations can describe the optical spectrum near the fundamental absorption threshold without significant corrections for solid-state effects. The molecular absorption (stick) spectrum computed for Alq is compared with the film measurements in Figure 2. The low-lying singlet states between 2.5 — 3.5 eV correspond to linear combinations of electronic excitations from an oxygen



**Figure 2: These calculations have given us an improved understanding of the molecular properties of Alq and how they extrapolate to the solid.**

atom to a nitrogen site on an individual quinolate ligand. The lowest triplet state lies  $\sim 0.65$  eV below the lowest singlet excited state.

Solid-state polarization corrections are not too important for the neutral excited states which appear in optical property calculations because the response of the environment to a local dipole is much less than

that for a charge. In contrast, large dielectric corrections must be included for the molecular calculations to describe the ionization potential and single particle energy gap. However, when these dielectric corrections are made, using the calculated molecular polarizability—which accurately gives the measured static dielectric constant—both the ionization potential and single particle energy gap are well described. The polarization stabilizes both the positive ion, thereby decreasing the ionization potential of the solid, and the negative ion, thereby increasing the electron affinity, relative to what would be measured or computed for the isolated molecule. Both effects therefore act to reduce the single particle energy gap. For the isolated molecule, the gap is calculated to be 5.8 eV; with polarization corrections this is reduced to 3.3 eV, in good agreement with the experimentally measured gap of  $3.0 \text{ eV} \pm 0.2 \text{ eV}$  [2].

We have made an initial attempt at understanding the electric field dependence of the electron mobility in this material using a model in which the mobility is dominated by hopping between molecules whose site energy distribution is governed by the randomly-oriented dipole moments of individual molecules. Such a model gives the appropriate (Poole-Frenkel) form for the mobility, and, using the calculated molecular dipole moment, a theoretical mobility within 50% of experiment at field strengths typical of device conditions.

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rlm@t12.lanl.gov  
Los Alamos