Combined Density Functional Tight Binding – Density Functional Theory Investigation of Effects of Nuclear Motion on Charge Transport in C60 and C70

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Fullerenes and fullerene-based materials are widely used as acceptor and electron transport layer materials in organic and planar perovskite solar cells. Ab initio modeling of electronic properties such as band alignment and charge transport for these applications is typically done using optimized geometries. Here, we estimate the effects of nuclear motions on band structure and electron and hole transport in two prototypical fullerenes, C60 and C70. We model the dynamics in solid fullerenes using Density Functional Tight Binding and we use the Density Functional Theory based Projection of Monomer Orbitals on Dimer Orbitals (DIPRO) approach to estimate effects on charge transfer integral in the Marcus approximation for the rate, $\omega_{ij} = \frac{|J_{ij}|^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}}exp\left[\frac{-(\Delta G_{ij}+\lambda)^2}{4\lambda k_B T}\right]$, where ω_{ij} is the charge transfer rate between states i and j (corresponding to "hopping" between frontier orbitals located at different molecular units), λ is the reorganization energy, ΔG_{ij} is the driving force, k_B is Boltzmann constant, and T is the temperature. J_{ij} is the overlap integral. We show that room-temperature molecular dynamics cause a shift and spread of frontier orbital energies on the order of 0.1 eV which leads to an increase by more than a factor of two in the Marcus exponent (expectation of $exp\left[\frac{-(\Delta E'-\Delta E''+\Delta G_{eq}+\lambda)^2}{4\lambda k_B T}\right]$, where $\Delta E'^{(\prime)}$ are deviations of frontier orbital energies due to dynamics, Fig. 1), and cause a decrease by up to orders of magnitude in the overlap integral, leading in this case to an overall decrease in the charge transport rate.

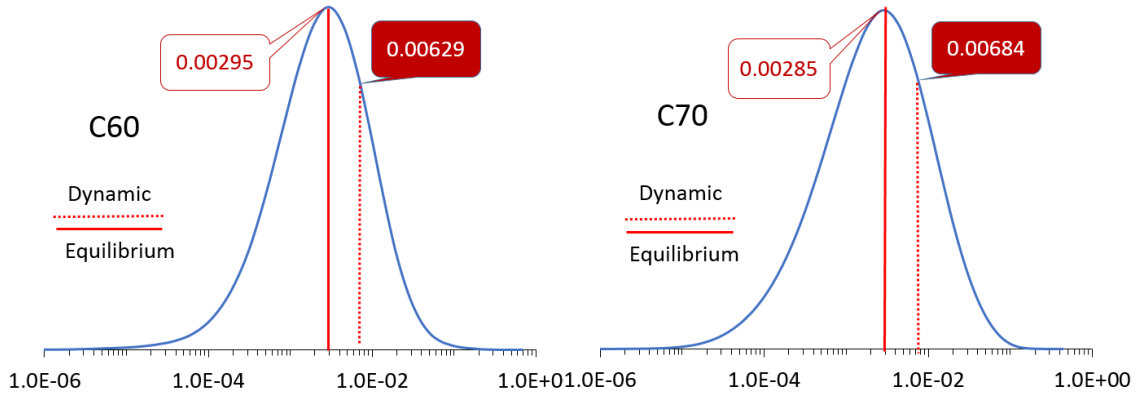

Fig. 1. The distributions of the values of the exponent in the Marcus equation ($exp\left[\frac{-(\Delta E'-\Delta E''+\Delta G_{eq}+\lambda)^2}{4\lambda k_B T}\right]$) for C60 and C70. The values at the equilibrium geometry and expectation values over molecular dynamics trajectories are indicated by solid and dotted red lines, respectively.