Quantum Localization and Delocalization of Charge Carriers in Organic semiconducting Crystals

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Exciting new technologies such as organic light emitting diodes, photovoltaics and nanoelectronics rely on organic semiconductors. While important progress has been made in recent years towards theoretical and computational modelling of organic semiconductors (OSs), understanding the charge transport (CT) mechanism in these materials is still very challenging because the parameters determining the dynamics are typically outside the regime of validity of existing theories (e.g. Hopping or Band theories). On the other hand, non-adiabatic molecular dynamics simulations are in principle free of model assumptions permitting an "ab initio" view into the CT mechanism. We have recently developed an efficient decoherence-corrected surface hopping methodology (denoted FOB-SH) which allows us to propagate the coupled electron-nuclear motion in realistic condensed phase systems [1-3]. Here we present the first application of FOB-SH (blue symbols Fig 1) to the calculation of room temperature charge mobility for a series of eight molecular organic crystals. We obtain very good agreement with experimentally measured mobility values over three orders of magnitude successfully bridging the regime where hopping (green symbols) and band models (red symbols) are invalid as shown in Fig 1. We find that the mechanism of transport critically depends on the ratio between electronic coupling and reorganization energy (electron-phonon coupling), V/λ. At small ratios, as found in p-MSB and naphthalene, the charge carrier is delocalized over no more than 1-3 molecules and diffuses through the crystal via slow hopping. For values exceeding the critical threshold $V/\lambda > 1/2$ as found in pentacene and rubrene, the charge carrier forms a polaron delocalized over 10 or more molecules concomitant with a strong increase in mobility. Implications of our work for the search of new organic materials with high room temperature mobility will be discussed.

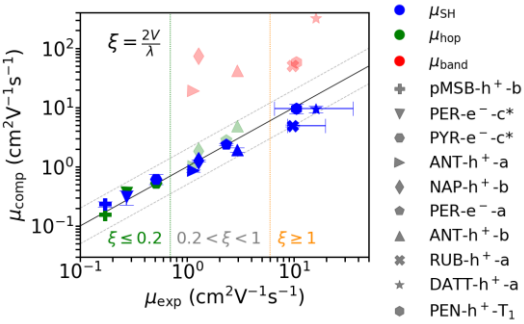

Figure 1: Comparison between computed and experimental (hole or electron) mobilities measured for eight organic semiconductors along different crystallographic directions. FOB-SH results are in blue, while hopping and band theory results are shown with green and red symbols respectively (shaded symbols represent regimes in which standard theories are no longer applicable).

References

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