Electron-phonon coupling and mobility modeling in organic semiconductors: a new and efficient methodology

P. Graziosi, R. G. Della Valle*, and E. Venuti*
Institute for Nanostructured Materials, National Research Council, via Gobetti 101, 40129, Bologna, Italy
*Department of Industrial Chemistry, University of Bologna, via Gobetti 85, Bologna, Italy
e-mail: patrizio.graziosi@cnr.it

ABSTRACT SUBMISSION

We have developed a first-principles method to calculate the electron-phonon coupling for specific modes and $\boldsymbol{q}$-points in the Brillouin Zone for crystalline organic semiconductors, which can be used to compute the corresponding mobility.

To validate our method, we compare the computed mobilities with available data for single crystals of naphthalene, anthracene and tetracene, finding a good agreement, especially when accounting for possible charged impurities.

INTRODUCTION

Organic Semiconductors (OSCs), based on abundant, eco-friendly, and cheap elements, have emerged as attractive candidates in several new electronic technologies. [1]

Two main approaches exist to describe charge transport in OCS: hopping and band transport via Boltzmann transport equation (BTE). The latter is particularly relevant for OSCs with orderly packed structures.

Here, we introduce a method to calculate and parametrize the electron-phonon coupling (EPC) in OSCs, and then use it to assess the mobility. We validate the overall method, Fig. 1, by comparing its results with experimental available data. [2]

MODEL

We employ DFT-VdW calculations using VASP, with the Phonopy package, to perform the simulations. The EPC at $\boldsymbol{q}$-point for phonon branch ν is computed as:

$$D_{\boldsymbol{q},\nu}^{n,n} = \frac{\partial t_W^n}{\partial \boldsymbol{r}_{\boldsymbol{q},\nu}} , \qquad D_{\boldsymbol{q},\nu}^{n,m} = \frac{\partial \Delta_s^{n,m}}{\partial \boldsymbol{r}_{\boldsymbol{q},\nu}} \qquad (1)$$

In (1), n and m are the band indexes, t_W^n is the transfer integral (¼ of the bandwidth) of band n, $\Delta_s^{n,m}$ the Davydov splitting between n and m, $\boldsymbol{r}_{\boldsymbol{q},\nu}$ the average displacements of all the atoms along the eigenmode ($\boldsymbol{q},\nu$). Then, we extract deformation potential values specific for band indexes and lattice phonon mode:

$$D_{n,m,\nu} = \frac{\sum_q {D_{\boldsymbol{q},\nu}^{n,m}}^2 DOS_{\boldsymbol{q},\nu}}{\sum_q DOS_{\boldsymbol{q},\nu}} \qquad (2).$$

The values in (2) are passed to the BTE solver *ElecTra* [3] to evaluate the charge mobility.

VALIDATION

The calculation of the Raman spectra, Fig. 2, allows to validate the description of the electronic and vibrational structures. The comparison with experimental single crystal mobilities, Fig. 3-5, shows a very good agreement, which improves when we consider possible ionized defects, Fig. 6. Importantly, the method is more than one order of magnitude cheaper than DFPT-based approaches.

CONCLUSIONS

A method has been developed and validated, that combines DFT-level calculations and semiclassical transport simulations to compute the electron-phonon coupling and charge mobility in organic semiconductors. The accuracy of the method improves when including defects.

ACKNOWLEDGMENT

We acknowledge the CINECA award under the ISCRA initiative, funding from the European Union–Next-Generation EU via the Italian call PRIN 2022, project code 2022XZ2ZM8, “POLYPHON” and from M.M.B. s.r.l., Faenza (RA) Italy for the VASP license.

REFERENCES

[1] Ö. H. Omar *et al.*, J. Mater. Chem. C 9, 13557 (2021).
[2] P. Graziosi *et al.*, Phys. Rev. Materials accepted, https://arxiv.org/abs/2407.18824.
[3] P. Graziosi *et al.*, Computer Physics Communications **287**, 108670 (2023).

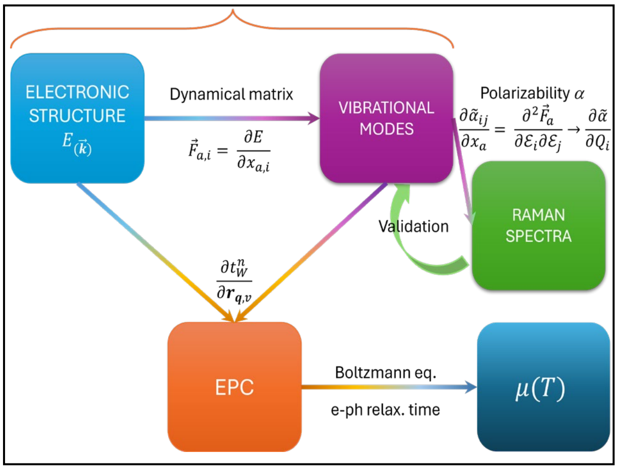

Fig. **1**. Scheme of the workflow from the electronic and phononic structure to the mobility μ.

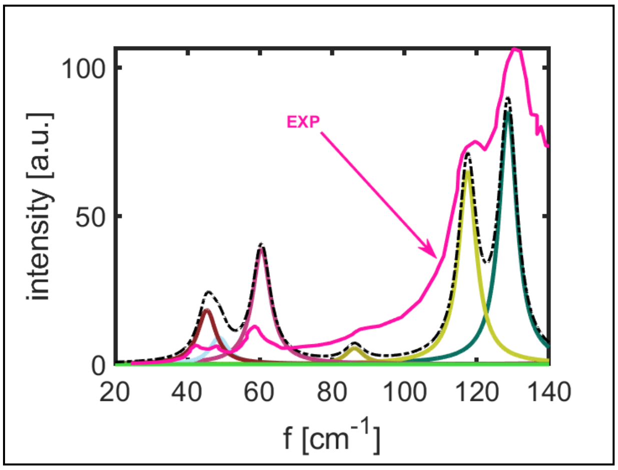

Fig. 2. Comparison of Raman spectra in the lattice phonons region of the bulk tetracene polymorph I; experimental (magenta) and computed (individual modes in colors and total in dash-dot black) spectra, ref. [3] and references therein.

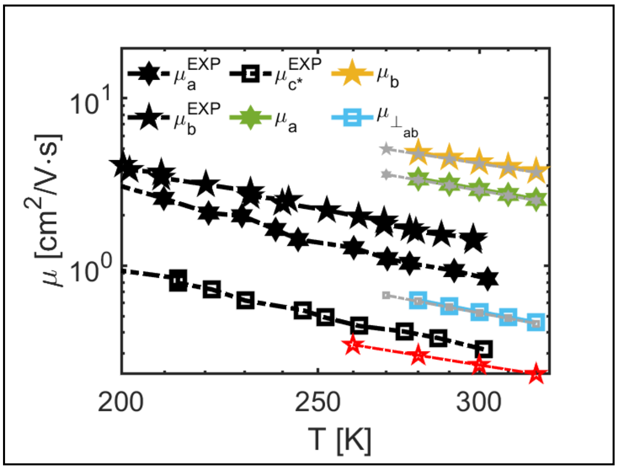

Fig. 3. Comparison of the hole mobility of naphthalene crystals along a, b, and $\perp_{ab}$ axes. In gray, elastic scattering with acoustic phonons is added; in red: μ_b from a computation based on DFPT which is ~ 30× more expensive, details in [3].

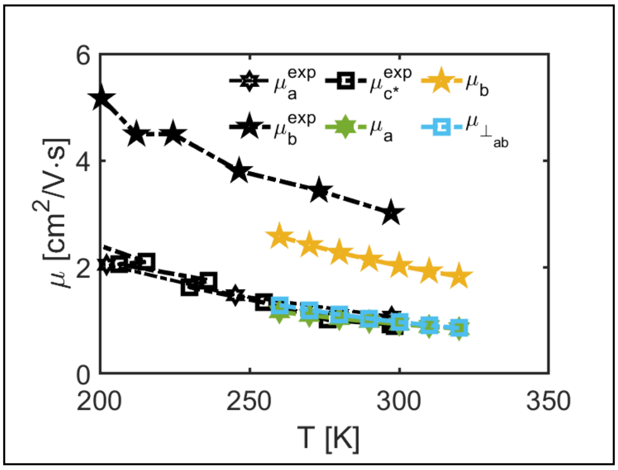

Fig. 4. Experimental and computed hole mobility of anthracene crystals along a, b, and c^* axes. [3]

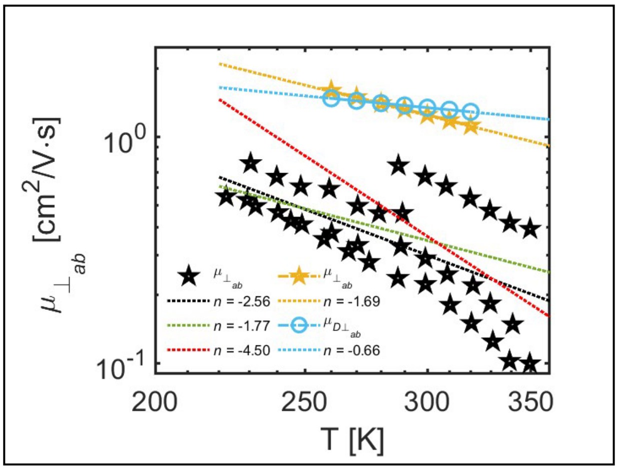

Fig. 5. Experimental vs computed hole mobility of tetracene crystals along the direction perpendicular to ab plane, $\mu_{\perp ab}$. The exponent of T^α fits are reported in the legend. μ_D is for the mobility evaluated from diffusivity via Einstein's relations. [3]

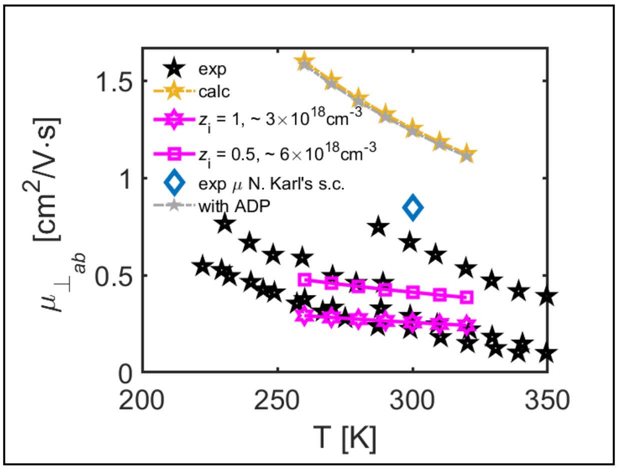

Fig. 6. Tetracene case as in Fig. 5, here magenta lines are for cases where scattering from ionized impurities of charge Z_i is included; Z_i = 0.5 mimics a charge spread over more sites, resembling extended charged defects, details in [3].