

Calculation of polarization energy in organic semiconductors upon addition of one hole or electron

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Organic semiconductor devices operate by the transfer of holes and electrons. In device performance, it is important to control the electronic levels, such as the HOMO level for hole conduction and the LUMO level for electron conduction. The electronic levels of organic solids are measured by photoelectron spectroscopy and inverse photoelectron spectroscopy, and they differ from those of isolated molecules due to various solid-state effects. One important solid-state effect is the interaction energy (polarization energy) between a charged molecule in a crystal and a polarized molecule in its vicinity. The polarization energy can be divided into two terms: Dynamic (D), which is the response of the charge distribution in the neutral molecule due to charge, and Electrostatic (S), which is the interaction between charge and the original charge distribution of the neutral molecule [1]. The purpose of this study is to theoretically calculate this polarization energy at the molecular level.

The electronic polarization D is approximated by charge-induced dipole and induced dipole-induced dipole interactions. The electrostatic interaction S is approximated by charge-permanent dipole and charge-permanent quadrupole interactions. The charged molecule was approximated as a point charge (+1e), and organic molecular spherical clusters centered on it were created and the bulk polarization energy was calculated based on Coulomb interactions. The polarization tensor and quadrupole tensor were calculated by Gaussian 16W HF_6-31g_d. The electric field created by the polarization of molecules around a point charge cannot be correctly represented by a single point dipole moment due to the influence of molecular shape and crystal structure (the self-consistent field equation was not converged), so the calculation was performed by reproducing the electric field by splitting the point dipole moment according to molecular shape. Calculations were performed for C60, pentacene, and perfluoropentacene. The calculation values can be divided into three terms: charge-induced dipole, induced dipole-induced dipole, and charge-permanent quadrupole. The charge-induced dipole term always has an energy that stabilizes the system, regardless of the sign of the charge (whether it is photoemission or inverse photoemission). The induced dipole-induced dipole term has a very small value compared to the other terms. The term charge-permanent quadrupole has the opposite sign of energy depending on the sign of the charge. The calculated total polarization energy is close to the value expected from the experiment, and its magnitude is roughly around 1 eV.

Reference:

[1] Y. Uemura, et al. Phys. Rev. B. **102**, 125302 (2020).