Anomalous Pressure Dependence of the Electronic Properties of Molecular Crystals Explained by Changes in Intermolecular Electronic Coupling

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Abstract: Optimization of the electronic properties of organic semiconductors is important for optoelectronic device applications. One method of tuning the electronic properties is applying external pressure on molecular crystals. A recent dispersion-inclusive density functional theory (DFT) investigation of the effect of pressure up to 20 GPa on herringbone polycyclic aromatic hydrocarbons (PAHs), has revealed anomalous pressure dependence of the electronic properties of six systems. Here, we use intermolecular electronic coupling values (H_{ab}), calculated by fragment orbital DFT (FO-DFT) to elucidate the pressure dependence of the electronic properties. We show that discontinuities in the pressure dependence of the band gap and direct-indirect band gap transitions are correlated with discontinuities in the pressure dependence of the electronic coupling of certain dimers, even when no discontinuities are found in the pressure dependence of the lattice parameters. H_{ab} is therefore a useful descriptor to gain insight into tuning the electronic properties of crystalline organic semiconductors.