Semi-empirically enhanced TD-DFT Spectra involving full Vibrational Progression for Morphology Characterization

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Exact knowledge of a (OPV-)device's morphology is key to fully understanding its properties. UV/Vis-spectra are commonly used for characterization of OPV-devices, often supplemented by quantum chemical calculations. The latter, however, almost always neglect vibrational progression (VP) which can be the main reason behind certain peak structures, thus resulting in poor agreement between theory and experiment.

Here, we present a straightforward semi-empirical procedure that utilizes the results of numerical fits of experimental data to account for VP in absorption spectra determined by TDDFT. This does not only present a comparatively simple way of improving the agreement between theory and experiment but also reduces the likelyhood of a peak being assigned to a transition despite originating from VP.

A conventional VP describes the intensities of the features caused by vibrational transitions from the lowest state in the ground-state potential to the lowest state in the excited state potential (0-0 features) and respective overtones. If only one electronic excitation is to be considered, the VP can be cast as eq. (1) [1].

$$(1) \qquad I_{\mathrm{abs}}(E) \propto \sum_{m=0}^{\infty} \frac{\mathrm{e}^{-S} S^m}{m!} \Gamma_w \left(E - E_{00} - m \cdot E_p\right)$$

Here, S, Γ_w, E_{00} are the Huang-Rhys factor, a Gaussian around 0 with FWHM $= w$ and the $0 - 0$ transition energy, respectively.

The figure below showing TDDFT (shifted by $-0.84\mathrm{eV}$) and experimental absorption spectra illustrates the benefit of this procedure as most of the structure in the low-energy transition is caused by VP. Additionally, the relative peak intensities of the curve obtained from our method show better agreement with the experiment.
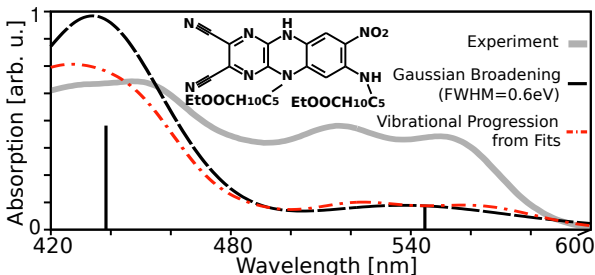
REFERENCES

[1] S. T. Hoffmann, H. Bässler and A. Köhler, What Determines Inhomogeneous Broadening of Electronic Transitions in Conjugated Polymers? *J. Phys. Chem. B* **114** (2010), 17037-17048.