UV-Vis spectra of organic dyes: unraveling the sources of band broadening

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Molecular materials have been under the spotlight for several decades due to their capacities of being used for photovoltaic and optoelectronic applications, accompanied by their lightweight and ease of chemical tuning from their organic nature.

While extensive experimental studies have been conducted on the photophysical properties of such systems, theoretical investigations often do not provide a complete depiction of the complexity of the mechanisms involved, and thus further studies are needed. Time-Dependent Density Functional Theory (TD-DFT) has been for the last few years routinely used to obtain by calculation the vertical absorption energies, while the reproduction of the UV-Vis spectra band shape received less attention. Aiming at calculated the UV-Vis bands in condensed phase, it is necessary to consider the different sources of broadening, i.e static disorder, vibronic coupling, temperature effect and/or exciton coupling.

This contribution will discuss the theoretical methodologies needed to simulate the different sources of broadening, in particular for the UV-Vis absorption bands of aromatic molecules in their crystalline phase. Using a QM/MM electrostatic embedding scheme as a first approach, static disorder can be simulated to reproduced experimentally seen broadening of UV-Vis spectra.[1] Vibronic contributions, which mainly contribute to the fine structure and dynamic disorder to the UV-Vis spectra can be obtained for molecular structures from first principles calculations, using a Fermi Golden Rule based formalism, leading to an estimation of the vibronic and temperature effects.[2] Discussions of the state of the art of calculations and limits will be discussed. Then, preliminary results of our studies on organic molecules and organic molecular crystals will be presented.

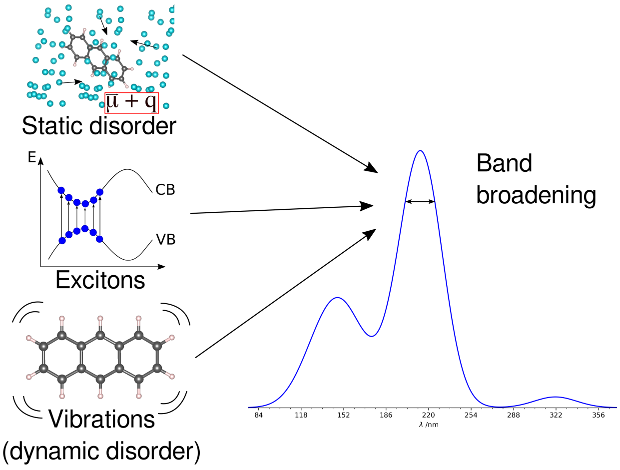

Figure 1: Sources of broadening in a molecular material.

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