Vibronic spectra for reduced-dimensionality models: Application to the Circular dichroism of chiral polythiophenes

D. Aranda[a], J. Cerezo[b], F. Ávila[a], F. Santoro*[c]
a) *Departamento de Química Física, Universidad de Málaga, 29071 Málaga, Spain.*
b) *Departamento de Química Física, Universidad de Murcia, 30100, Murcia, Spain,*
c) *Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), 56124 Pisa, Italy.*

Methods to compute vibronic spectra of rigid systems are mature enough to become standard[1,2], however, when modelling complex systems is convenient to consider one part that represent the "true" system (i.e. chromophore in a protein), even though it may not be a minimum of the reduced system. This poses the problem of computing a vibronic spectrum of a system out-of-equilibrium. One possibility to solve this issue is to remove the degrees of freedom affected by the neglected part. Recently, we worked out a novel protocol in internal curvilinear coordinates to deal with these situations[3]. We have selected polythiophenes (PT) as model because of the complexity of their multiple anharmonic inter-ring torsions. In spite of having been widely studied, the origin of their circular dichroism (ECD) spectrum is still up for debate. It has been shown that oligomer stacked chains forming a supramolecular helix can explain the shape of the ECD spectrum[4]. By the other hand, experimental data from a single PT derivate molecule[5] show similar results. In this work, we studied all-anti/all-syn single chain oligothiophenes with different sizes and torsion angles as model using quantum mechanical calculations based on the Density Functional Theory (DFT). Whereas all-anti chains show a strong monosignated ECD in the range of study - which correspond to the first excited state, S_1 - all-syn chains possess another bright state slightly higher on energy (S_2 in our model) with opposite sign to S_1. The coupling of the contributions of the two states give rise to a ECD spectrum in good agreement with experiment (Figure 1).
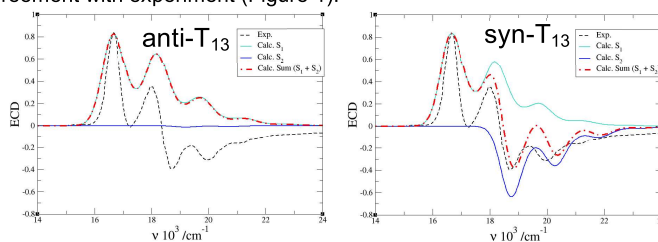

Figure 1. Calculated Vertical Gradient Frank-Condon spectra for the T_{13} model compared with experimental results. Calculated spectra were fitted with the lowest energy peak.

References
1. F. Avila, F. Santoro, *Phys. Chem. Chem. Phys.* 2012, **14**, 13549.
2. J. Cerezo, F. Santoro, *J. Chem. Theory Comput.* 2016, **12**, 4970.
3. J. Cerezo, F. Santoro et al, unpublished.
4. D. Padula, F. Santoro, G. Pescitelli, *RSC Adv.* 2016, **6**, 37938.
5. C. Li, M. Numata, A. Bae, K. Sakurai, and S. Shinkai, *J. Am. Chem. Soc.* 2005, **127**, 4548.