THE INVESTIGATION OF STEREOSPECIFIC INTERMOLECULAR INTERACTIONS THROUGH VIBRATIONAL CIRCULAR DICHROISM (VCD) IN THE IR AND IN THE NIR

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Vibrational Circular Dichroism (VCD), in combination with DFT calculations, has proven through the years as a very sensitive technique to assign the absolute configuration and to investigate the conformational landscape of small to medium size molecules or of organometallic complexes [1]. Also the secondary structure of macromolecules has been successfully studied, through more approximate modelling, even in presence of fibrillar aggregates [2].

However, VCD can be quite effective also to understand helicization phenomena for extended organic delocalized π-systems, promoted by the presence of Ag and other transition metal ions, see ref. [3]. We will report on studies of ad-hoc designed rather large systems, in which the central role of the ions in driving helicization is evidenced.

The technique, in the fundamental OH-stretching IR region and in the less investigated first overtone NIR region, is quite valuable to investigate intra-molecular and even inter-molecular hydrogen bonding phenomena in alcohols and diols [4], where the computational price to pay is accounting for the rather large anharmonic contributions. We will illustrate here also the case of amino-alcohols, where the NIR region proves even more useful, due to the higher relative intensity of the first overtone spectra.

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[2] Timothy A. Keiderling. Structure of Condensed Phase Peptides: Insights from Vibrational Circular Dichroism and Raman Optical Activity Techniques. *Chem. Rev.* 2020, *120*, 3381-3419.

[3] Pablo Reiné, Ana M. Ortuño, Sandra Resa, Luis Álvarez de Cienfuegos, Victor Blanco, M. José Ruedas-Rama, Giuseppe Mazzeo, Sergio Abbate, Andrea Lucotti, Matteo Tommasini, Santiago Guisán-Ceinos, Maria Ribagorda, Araceli G. Campaña, Antonio Mota, Giovanna Longhi, Delia Miguel, Juan M. Cuerva. OFF/ON switchingof circularly polarized luminescence by oxophilic interaction of homochiral sulfoxide-containing o-OPEs with metal cations. *Chem. Comm.* 2018, 54, 13985-13988.

[4] Lorenzo Paoloni, Giuseppe Mazzeo, Giovanna Longhi, Sergio Abbate, Marco Fusè, Julien Bloino, Vincenzo Barone. Toward Fully Unsupervised Anharmonic Computations Complementing Experiment for Robust and Reliable Assignment and Interpretation of IR and VCD Spectra from Mid-IR to NIR: The Case of 2,3-Butanediol and trans-1,2-Cyclohexanediol. *J. Phys. Chem. A* 2020, *124*, 1011-1024.