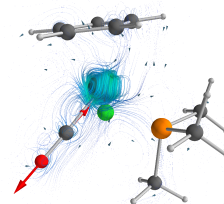


ANHARMONICITY AT LARGER SCALES: VIBRATIONAL SPECTRA OF CHIRAL ORGANOMETALLIC COMPLEXES

JULIEN BLOINO, *Scuola Normale Superiore, Scuola Normale Superiore, Pisa, Italy*; MARCO FUSÈ, *Department of Molecular and Translational Medicine, University of Brescia, Brescia, Italy*.

Beyond their central roles in some enzymes and proteins, chiral organometallic complexes have potential applications in synthetic drugs, as biomarkers or in catalysis for instance. Their structural characterization can help rationalize their activity, including their bioactivity and toxicology. Experimentally, a key role is played by vibrational spectroscopies like IR and Raman scattering, with a more comprehensive picture achieved by the use of their chiroptical counterparts, respectively vibrational circular dichroism (VCD) and Raman optical activity (ROA).[1] Because of the complexity of the signal, the interpretation of chiral spectra needs to be assisted by computations.

However, chiral spectroscopies are characterized by a higher sensitivity and low-intensity spectra (typically 4-5 orders of magnitude lower than the non-chiral ones), so standard protocols rooted into the density functional theory within the harmonic-oscillator approximation can be insufficient. A straightforward path of improvement is the inclusion of anharmonicity, but the typical size of organometallic compounds is generally too large even for relatively cheap methods such as the second-order vibrational perturbation theory (VPT2). On the other hand, a full anharmonic treatment may be unnecessary to investigate probe vibrations or specific spectral regions. Indeed, a model system can be built by considering the anharmonic contributions only for a subset of relevant modes without loss of accuracy. In this contribution, we will discuss how this can be done and analyze the potential pitfalls. Finally, we will show how computations can be used to provide new visual insights on the local origin of the observed bands.[2]



[1] T. Wu, X.-Z. You, P. Bouř, *Coord. Chem. Rev.* 2015, **284**, 1-18

[2] a) L. A. Nafie, *J. Phys. Chem. A* 1997, **101**, 7826; b) M. Fusè, F. Egidi, J. Bloino, *Phys. Chem. Chem. Phys.* 2019, **21**, 4224-4239