Decoding chemical information from vibrational spectroscopy data: Local vibrational mode theory

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The local vibrational mode theory originally introduced by Konkoli and Cremer has becomes over the past years a versatile tool for the characterization of chemical bonding and/or weak chemical interactions. [1] Local mode stretching force constants are a unique measure of the intrinsic bond strength in contrast to normal mode stretching force constants, which suffer from the fact that normal vibrational modes are generally delocalized in polyatomic systems. [2] Local and normal vibrational modes are linked through an adiabatic connection scheme, which has led to a new comprehensive analysis of IR/Raman spectra via the decomposition of normal modes into local mode contributions. [3]

After a short introduction of the theoretical background, we will present some recent examples stretching from long covalent CC bonds, metal-ligand bonding in sandwich complexes and hemeproteins to bonding in ruthenium releasing nitrile drugs, followed by an application of the normal mode decomposition procedure. [4-6]

Finally, we will present the open-source local mode program LModeA [1] which can easily be applied after a routine quantum chemical calculation of vibrational frequencies but also to measured vibrational frequencies, with moderate computational costs.

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