Anharmonic Theoretical Vibrational Spectroscopy with Localized Modes

Pawel T. Panek[1] and Christoph R.Jacob[2,*]

[1]*TU Braunschweig, Institute of Physical and Theoretical Chemistry, Hans-Sommer-Str. 10, 38106 Braunschweig, Germany*

[*]*Corresponding author:* c.jacob@tu-braunschweig.de

Quantum-chemical calculations of the vibrational spectra for large molecules, such as polypeptides or clusters, are usually restricted to the harmonic approximation. However, anharmonic contributions can impact the vibrational spectra significantly and are essential for describing two-dimensional infrared (2D-IR) experiments. Unfortunately, computational methods for treating anharmonicities show a steep increase of the computational cost with system size, which limits their applicability to small molecules.

In this talk, we will present an efficient approach for the calculation of anharmonic vibrational spectra of large systems. We demonstrate that instead of the commonly used normal mode expansion of the potential energy surface, localized modes [1] should be used as starting point for the treatment of anharmonicities. In this space, we perform Local Vibrational Self- Consistent Field (L-VSCF) and Local Vibrational Configuration Interaction (L-VCI) calculations [2]. We show that in this case, many couplings between local modes can be neglected without significant loss of accuracy. This provides a route to the efficient and reliable calculation of anharmonic vibrational spectra of large (bio-)molecules.

This allows for an efficient inclusion of anharmonic contributions in quantum-chemical calculation of vibrational spectra for small organic molecules [3] and for helical alanine polypeptides [4]. For the latter, anharmonic infrared, Raman, and Raman optical activity spectra are presented and the impact of anharmonicities on the vibrational spectra is discussed.

Acknowledgments: We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for funding via Grant JA 2329-2/1 and acknowledge support from COST CMST-Action CM1405 Molecules in Motion (MOLIM).

References

[1] Ch. R. Jacob, M. Reiher, *J. Chem. Phys.* 2009, **130**, 084106.
[2] P. T. Panek, Ch. R. Jacob, *ChemPhysChem* 2014, **15**, 3365-3377.
[3] P. T. Panek, Ch. R. Jacob, *J. Chem. Phys.* 2016, **144**, 164111.
[4] P. T. Panek, Ch. R. Jacob, *J. Phys. Chem. Lett.* 2016, **7**, 3084-3090.