ACCURATE ANHARMONIC IR SPECTRA FROM INTEGRATED CC/DFT APPROACH

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The recent implementation of the computation of infrared (IR) intensities beyond the double harmonic approximation [1] paved the route to routine calculations of infrared spectra for a wide set of molecular systems. Contrary to common beliefs, second-order perturbation theory is able to deliver results of high accuracy provided that anharmonic resonances are properly managed [1,2].

It has been already shown for several small closed- and open shell molecular systems that the differences between coupled cluster (CC) and DFT anharmonic wavenumbers are mainly due to the harmonic terms, paving the route to introduce effective yet accurate hybrid CC/DFT schemes [2]. In this work we present that hybrid CC/DFT models can be applied also to the IR intensities leading to the simulation of highly accurate fully anharmonic IR spectra for medium-size molecules, including ones of atmospheric interest, showing in all cases good agreement with experiment even in the spectral ranges where non-fundamental transitions are predominant[3].

[1] J. Bloino and V. Barone, J. Chem. Phys. 136, 124108 (2012) [2] V. Barone, M. Biczysko, J. Bloino, Phys. Chem. Chem. Phys., 16, 1759-1787 (2014) [3] I. Carnimeo, C. Puzzarini, N. Tasinato, P. Stoppa, A. P. Charmet, M. Biczysko, C. Cappelli and V. Barone, J. Chem. Phys., 139, 074310 (2013)