A Virtual Spectrometer to Predict and Interpret Vibrational Spectra

Julien Bloino[a] and Vincenzo Barone[a]

[a]*Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy*
julien.bloino@sns.it

Computational spectroscopy is nowadays routinely used as a predictive and interpretative tool to complement and support experiment, providing insights of the underlying elementary phenomena responsible for the overall band-shape. However, the reliability of the produced results is strongly correlated to the underlying models. This aspect can be especially critical in some fields of applications like chiroptical analysis or astrochemistry, for instance. Such considerations emphasize the need of carefully setting up computational protocols, in particular by selecting the most appropriate level of theory available. As a matter of fact, for medium-to-large molecular systems with possible environmental effects, a trade-off is necessary between accuracy and computational cost, and several strategies can be devised, with suitabilities varying depending on the cases.
To facilitate the setup of the most efficient and reliable route for the simulation of accurate spectra, we have been developing a versatile and modular platform, called virtual spectrometer [1,2]. In this contribution, we will illustrate the possibilities offered by such a tool as a versatile companion to experiment, with emphasis on vibrational spectroscopy. Thanks to modern processing powers, the systematic or tailored inclusion of anharmonic contributions, even for medium-to-large molecules, has become possible. Despite their undeniable worth[3-5], the inherent complexity of anharmonic models, coupled to their sensitivity to the underlying electronic structure calculations, represents a serious hurdle to a broader application. Focusing on the second-order vibrational perturbation theory (VPT2)[6], we will present some of its pitfalls and highlight how robust protocols can be designed and automatized to build friendlier tools requiring minimal input from the user.[2] Finally, by choosing a suitable representation, intermediate data produced during simulations can be exploited to assess the reliability of the results and provide further insights into the origin of the observed signal.[7]

References

1. V. Barone, A. Baiardi, M. Biczysko, J. Bloino, C. Cappelli and F. Lipparini, *Phys. Chem. Chem. Phys.*, **14** (2012), 12404.
2. J. Bloino, A. Baiardi and M. Biczysko, *Int. J. Quantum Chem.* **116** (2016), 1543.
3. M. Biczysko, J. Bloino and C. Puzzarini, *WIREs Comput. Mol. Sci.* **8** (2018) e1349.
4. N. M. Kreienborg, J. Bloino, T, Osowski, C. H. Pollok and C. Merten, *Phys. Chem. Chem. Phys.* **21** (2019), 6582.
5. C. Puzzarini, J. Bloino, N. Tasinato, and V. Barone, *Chem. Rev.* **ASAP** DOI: `10.1021/acs.chemrev.9b00007`
6. H. H. Nielsen, *Rev. Mod. Phys.* **23** (1951), 90.
7. M. Fusè, F. Egidi, J. Bloino, *Phys. Chem. Chem. Phys.* **21** (2019), 4224.