Modeling of Molecular Vibrations: Current Challenges and Future Perspectives

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ABSTRACT

Spectroscopies, such as Infrared and Raman, are very powerful tools for the investigation of physical-chemical properties of molecular systems, providing detailed information related to the structure and dynamics. However, experimental spectra are tuned by several intertwined effects which can make the interpretation of experimental data very challenging without the support of reliable *in silico* simulations.

The main of this presentation is to provide an overview of theoretical models and computational strategies for the simulation of vibrational spectra. The first part will focus on the simulation at the harmonic level, highlighting its main limitations. Then, a general overview of the approaches for the inclusion of anharmonic effects will be presented In particular, the vibrational second-order perturbation theory (VPT2) has shown to offer a very effective balance between accuracy and computational cost, allowing the treatment of medium-to-large size molecular systems. In this context, the problem of degenerate vibrations, characterizing high-symmetry systems, will be addressed as well.

The second part of the presentation will focus on the treatment of molecules presenting highly-anharmonic, floppy large amplitude motions (LAMs), which are unsatisfactorily described at the purely VPT2 level. In this case, one of the most promising strategies is based on an interplay between different approaches aimed at treating each vibration through the most appropriate method.

In order to prove the reliability of all the models, several applications to the simulation of Infrared and Raman spectra will be presented, taking molecular systems of biological and astrochemical interest as test-cases.

REFERENCES

1. H. H. Nielsen, *Rev. Mod. Phys.* 23. (**1951**). 90.
2. V. Barone, *J. Chem. Phys.* 122. (**2005**). 014108.
3. V. Barone, J. Bloino, C. Guido, F. Lipparini, *Chem. Phys. Lett.* 496. (**2010**). 157.
4. V. Barone, *Computational Strategies for Spectroscopy, from Small Molecules to Nano Systems*, John Wiley & Sons, Inc., **2011**.
5. J. Bloino, M. Biczysko, V. Barone, *J. Chem. Theory Comput.* 8. (**2012**). 1015.
6. M. Piccardo, J. Bloino, V. Barone, Int. J. Quantum Chem. 115. (**2015**). 1948.
7. M. Mendolicchio, J. Bloino, V. Barone, *J. Chem. Theory Comput.* 17. (**2021**). 4332.
8. Q. Yang, M. Mendolicchio, V. Barone, J. Bloino, *Front. Astron. Space Sci.* 8. (**2021**). 77.