Molecular conformation from vibrational spectra: anharmonicity is key!

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Molecular structure determination from vibrational data is still a very difficult problem, mostly due to the large number of close-lying transitions that occur for systems of a chemically relevant size. As experimental investigations become more complex and the size of the systems studied increases, there is a pressing need for a reliable theoretical framework that can help assign the lines observed by spectroscopists and thus facilitate structure elucidation from vibrational data.

Unfortunately, the current standard theoretical model of molecular vibrations, namely the harmonic approximation, is unable to capture some of the key vibrational phenomena. Indeed, most of the modern spectroscopic experiments that deal with energy transport, conformational transitions, non-linear spectra, or dissociative excitations fall outside the remit of this approximation.

Over the years, we have developed a series of theoretical techniques [1–5] that go beyond the harmonic approximation and allow us to perform fast and accurate quantum mechanical vibrational calculations on molecular systems, using interaction potentials computed directly by electronic-structure programs and grid-computing technology.

In this contribution, we focus on the determination of the conformation of small biological molecules and model proteins with the aim of understanding the subtle balance of weak interactions leading to the formation of nano-scale biostructures. We use our latest methodology to interpret high-resolution spectra of gas-phase biomolecules, and highlight the importance of anharmonicity for a reliable determination of molecular conformations from vibrational data.

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