

Vibrational solvatochromism from first principles - new insights

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ABSTRACT: Many simple semi-empirical models of vibrational solvatochromism reported so far were able to successfully describe, in some special cases, the vibrational response of small infrared probes due to external environment. However, modeling the effects of intermolecular interactions on the vibrational frequencies is challenging because they are quantum mechanical in nature. In fact, the existing models are generally not acceptable in some important cases because they are strictly electrostatic.

Throughout the recent years, we have been developing the rigorous first-principles theory of vibrational solvatochromism of spatially localized infrared probes that are the reporters of the nearest molecular environments and can provide crucial information about the structure and dynamics of biomolecules. In this presentation, we discuss the capability of our approach to reproduce experimental frequency shifts of model IR probes. In particular, we explain the observed breakdown of electrostatic models applied to nitrile stretch vibrational modes in H-bonding environments. We also provide the scope of further development and possible limitations of our method.

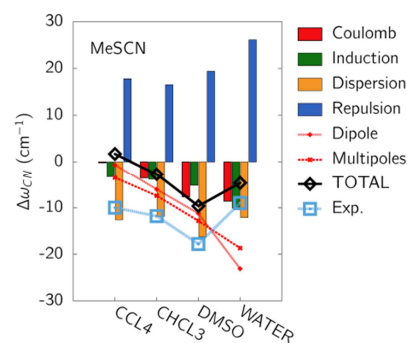


Fig. 1. Breakdown of electrostatic model in water.

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