

On the Synergy of Matrix-Isolation Infrared Spectroscopy and Vibrational Configuration Interaction Computations

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Numerous developments in quantum chemistry promise an economic and flexible, yet, accurate access to Potential Energy Surfaces (PESs) of polyatomic molecular systems, where the design of global PESs is cumbersome and expensive. A prominent field where accurate PESs are needed is Vibrational Structure Theory, *e.g.*, for the calculation of vibrational states of molecular systems by variational methods for solving the time-independent nuclear Schrödinger equation, *i.e.*, Vibrational Self Consistent Field (VSCF) and Vibrational Configuration Interaction (VCI). Within a variety of authors working in this field, we find the most versatile implementations in the MOLPRO software package [1] with the PES generator and VSCF/VCI algorithms by Rauhut et al. [2,3]. In this work, we recorded high-resolution spectra by Argon and Neon Matrix-Isolation Infrared (MI-IR) Spectroscopy, a technique that suppresses molecular rotation to access pure vibrational spectra. We perform VSCF/VCI computations on *ab initio* multi-mode PESs to support assignment of the MI-IR spectra, which, vice versa, validate the accuracy of the computations. With this iterative spectroscopic characterization, we are able to solve some inconsistencies in the well-studied spectrum of the water monomer [4] and to confirm the experimentally implied molecular picture by quantum chemical calculations. We extend this combined experimental and computational approach to compounds, where a precise characterization is highly relevant, *e.g.*, key components in the activation of carbon dioxide or volatile organic compounds found in the atmosphere.

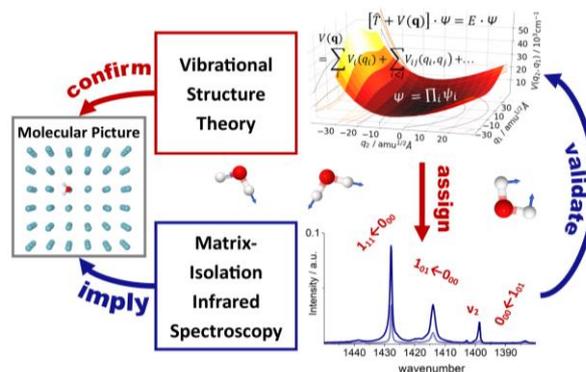


Figure 1: Schematic representation of the iteration between theory and experiment that take place during characterization of molecules by spectroscopy.

References

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