

COLD ION SPECTROSCOPY AND BOMD: TOWARDS UNCOVERING THE ORIGIN OF MYSTERIOUS PEAKS

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Density functional theory is a common tool for calculating infrared (IR) spectra. While harmonic approximation usually performs well on the molecules of small to medium size, it fails for predicting IR spectra of large ions. On the other hand, classical anharmonic treatment such as VPT2 or VSCF, becomes prohibitively expensive for large molecules.

An alternative approach is to calculate the IR spectrum by the Fourier transform of the dipole moment autocorrelation function from a classical trajectory,[1] e.g., from Born-Oppenheimer molecular dynamics (BOMD). In contrast to the harmonic approximation, BOMD includes the vibrational couplings as well as conformational sampling at a given temperature.

In the Chen group, we have recently started studying IR spectra of large ions in the gas phase.[2] In order to understand the complicated IR fingerprints of those systems, we investigated the possibility of calculating IR spectra by BOMD simulations with the semi-empirical GFN-xTB methods,[3,4] and used this approach in combination with DFT to understand experimental IR spectra.

References:

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