

EFFECT OF ANHARMONICITY ON ADSORPTION THERMODYNAMICS

Low frequency modes can make a sizable contribution to the binding free energy computed using the **harmonic oscillator approximation** (HO), but is even appropriate to use the HO-expression for the free energy for these modes. In a paper I highlighted previously, Kjærgaard and co-workers showed that the HO gave good agreement with the experimental binding free energy for acetonitrile-HCl dimer even though the lowest frequency mode was a mere 38 cm^{-1} .

However, in this study Piccini and Sauer show that anharmonic effects need to be included to obtain agreement with the experimental binding free energy of methane to H-CHA zeolite. Specifically, Piccini and Sauer compute the vibrational binding free energy by computing the 1-dimensional (1D) PES for each low frequency mode and compute the vibrational energy levels and corresponding partition function numerically using the method proposed by Beste (as opposed to using the anharmonic fundamental frequency together with the HO partition function). This decreases the binding free energy by 2.5 kcal/mol compared to the standard HO treatment.

Actually, Piccini and Sauer show that the usual double difference displacement in Cartesian coordinates can result in errors for low frequency modes and if harmonic frequencies are extracted from the 1D PESs the difference between harmonic and anharmonic binding free energies increase to 3.0 kcal/mol. (Of course if one has already computed the 1D PESs one might as well compute the anharmonic free energy contribution).

As Piccini and Sauer point out it is crucial to use internal coordinates when displacing the molecule along the normal mode to minimize unphysical distortions in bond lengths and bond angles. The choice of internal coordinates can affect the results and must be chosen carefully.

One note on the general methodology (described in more detail here): I believe the normal mode optimization reduces to a standard RFO quasi Newton-Raphson optimization if all modes are optimized, but using a transformed gradient rather than the Cartesian gradient to check convergence. So if one is using such an optimizer to begin with (rather than e.g. conjugate gradient) implementing the normal mode optimization is not necessary or requires merely a change in convergence criteria.

Source: <http://www.compchemhighlights.org/2015/02/effect-of-anharmonicity-on-adsorption.html>