From adsorptation to dissipation: insights from computer simulations of solid H2O and CO

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Summary

Microscopic interactions are characterized through atomistic simulations using either first principals quantum chemistry techniques or empirical interatomic potentials. Understanding these microscopic interactions helps us understand large scale phenomena such as catalysis, crystal growth, and phase transitions. In particular, the processes of adsorption and vibrational energy relaxation (VER) are intrinsically related to catalysis. Adsorption is the first step in a catalytic process, and VER is often the rate limiting step in a catalytic cycle. Thus, understanding the microscopic interactions that govern adsorption and VER is crucial to understanding catalysis.

Adsorption

Adsorption is the process by which molecules or atoms adhere to a surface, over time forming a thin film or layer. Experiments offer the most realistic value for the binding energy, however, they can only measure the statistical average binding energy. Similarly, experimental measurements of adsorption are often unable to provide realiable data on certain unique cases. This is due to the fact that measurements of binding energies tend to rely on the desorption of the adsorbed molecules at a certain termperature. Hence, the unique case of a molecule adsorbing on a solid of the same species (*ie.* H_2O on H_2O) with a binding energy larger than the cohesive energy is nearly impossible to measure. Simulations can fill in the gaps by providing a complete distribution of the binding energies, including the unique case mentioned above.

Vibrational Energy Relaxation

Vibrational energy relaxation (VER) is the process by which a vibrationally excited molecule returns to its ground state by transferring its excess energy to its surroundings. This process is crucial in many chemical and physical phenomena, including energy transfer in biological systems, catalysis, and in the selectivity of chemical reactions. VER can occur through various mechanisms, including vibrational-vibrational (V-V) energy transfer, vibrational-translational (V-T) energy transfer, vibrational-rotational (V-R) energy transfer, and vibrational-electronic (V-E) energy transfer. The efficiency of VER depends on several factors, including the nature of the molecule, the surrounding environment, and the energy gap between the excited and ground states.

The most common way to study VER in simulations is to use non-equilibrium molecular dynamics (NEMD) simulations. In these simulations the molecule of interest is excited to a higher vibrational state, and the subsequent relaxation process is monitored over time. A general trend for VER lifetimes is that they decrease with increasing temperature, a result of an increased coupling between the excited molecule and the surrounding bath modes. This increased coupling is due to the fact that higher temperatures lead to higher occupancy of vibrational modes within the bath, effectively reducing the energy gap.

This Thesis

Chapter 3: A Julia package for atomic simulations, *YetAnotherSimulationSuite.jl* (YASS), that was developed during the PhD is described. Benchmarks comparing the performance of this package to the most popular Python-based package (ASE) are shown. The Julia package is up to 6 times faster, with initial compilation time overhead making it slower for very short calculations. As the calculation times grows the speedup offered by the Julia package also grows.

Chapter 4: The binding energy of H_2O on the ice Ih (0001) surface is studied. The physiochemical properties governing the adorption are broken down and carfeully scrutinized. We find an abundance of binding sites with binding energy larger than the cohesive energy of the crystal. This has significant implications for crystal growth, where the standard model is no longer applicable. Furthermore, we explore how the local environment on the surface influences the binding energy. From this we produce a descriptor for the local surface environment that can be used to predict the binding energy at sites on the surface.

Chapter 5: The binding energy of CO on amorphous and crystalline CO is studied. The most important contributions to the binding energy are investigated, and the importance of long-range interactions is analyzed. Furthermore, a benchmark of DFT functionals is carried out, where the best performing functional is presented. We find that CO binding is dominated by dispersion, with negligible contributions from many-body effects in solid CO. The distribution of binding energies for CO on amorphous CO is broad (200 − 1600 K), and depends on the size of the cluster. The dependence on the size of the cluster reveals that long-range interactions are relevant to the adsorption of CO on amorphous CO. Zero point energy corrections within the harmonic approximation lowers the average binding energy by 20-30%. CO binding on crystalline α-CO has a narrower distribution (650 − 800 K), and is orientation dependent. The median value of the binding energy distribution for amorphous and crystalline CO are very similar, corroborating previous studies which assumed them to be equal. Lastly, a benchmark revealed that the ωB97M-V functional performs the best when treating the CO–CO dimer interaction energy.

Chapter 6: Utilizing NEMD simulations the VER process for CO in amorphous and crystalline CO is studied. A novel analysis techinique for studying the frequency-gap dependence of the decay time constant was developed. Anharmonic coupling between an excited CO molecule and a different CO isotopologue results in vibrational energy relaxation (VER) that is faster when the excited molecule has a lower frequency than the accepting molecule. Whereas, in crystalline clusters the frequency-gap dependence exhibited no significant trends other than being most efficient at gaps of 50 cm^{-1}. Vibrationally excited CO molecules in solid CO redistribute their energy primarily through vibrational–vibrational energy transfer. This is due to the large frequency-gap between the vibrational mode of CO and the rotational and phonon modes of CO clusters. The CO VER exhibits a two-channel decay dependence on the frequency-gap, analogous to the quantum mechanical prediction of CO VER switching from one-phonon to two-phonon assisted decay. The necessary physiochemical properties for VER are well captured by the classical pair potentials used to simulate the VER of CO.

Outlook

The collection of works within this thesis not only presents novel results, but also opportunities for furture works to continue advancing our understanding of the topics studied. In the works published much earlier, some of these new opportunities have already been taken and subsequent papers have been published by others. In particular, the results found in Chapter 5 & Chapter 6 have been used to explain experimental results that offer some understanding of observed gas-phase CO abundances in the ISM. Furthermore, *YetAnotherSimulationSuite.jl* can continue to grow and mature as an open-source package. As it attracts more user and developer attention it can grow to be of significant importance to the computational chemistry community.