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

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Chapter 1

Introduction

Scientific research often comes in two forms, experimental and theoretical, where the former consists of laboratory measurements and the latter comes from mathematical formulations. These two disciplines maintain a symbiotic relationship, where experimental work is often used to verify approximate theoretical models and theoretical works are able to fill in knowledge gaps due to technical limitations in experiments. The work in this thesis focuses primarily on computer simulations based on approximations for atomic-scale interactions, with an emphasis on properties or processes that experiments are unable to observe.

Atomic-scale interactions are described using either first-principles quantum chemistry techniques or empirical interatomic potentials. These atomic-scale interactions are important because they govern the macroscopic properties of materials. Understanding these atomic-scale 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 important for determining the next elementary reaction step in a catalytic cycle. Thus, understanding the atomic-scale interactions that govern adsorption and VER at the atomic-scale is crucial to understanding catalysis. In this thesis I study adsorption and VER for two simple yet interesting molecules, carbon monoxide (CO) and water (H_2O).

Carbon Monoxide

CO is one of the most abundant molecules in the interstellar medium (ISM).[1–3] In the ISM CO is known to form in the gas phase, where it then condenses onto icy grains.[4] On these icy grains CO is thought to be the seed for the formation of various other molecules, such as CO_2[5], CH_3OH[6,7], and logically all other molecules formed by reactions with CO_2 or CH_3OH. Furthermore, due to the CO being an extremely volatile species, sublimating at 25 K, it is the perfect measure of the degree of thermal processing of icy grains. To physical chemists, CO is of high interest due to its vibrational energy pooling (VEP) properties, most notably when adsorbed on a sodium chloride crystal.[8–10] CO is the perfect candidate for studying vibrational energy transfer. Given it only possesses a single molecular vibrational mode, which has a large energy gap from its lattice modes, CO can easily be used to study how vibrational energy is transferred. Isotopic studies can be used to quantify the effect of the energy gap on the efficiency of energy transfer.

Water

Water is one of the most extensively studied molecules in existence. It has earned this title not only by being vital to life but also due to its unique properties (high heat capacity, inverse thermal expansion, etc.). As a liquid water serves as a universal solvent for biochemical processes, whereas, in solid form it serves as a catalyst for reactions in the ISM. In nearly all domains of chemistry water is an essential and highly studied molecule. Despite this, to this day there still remains numerous unexplained phenomena revolving around water, one of which is investigated in Chapter 4.

1.1 Computer Simulations

Molecular simulations rely on statistical mechanics and numerical methods to simulate molecular systems at various length and time scales. The work presented in this thesis focuses on atomic simulations using interatomic potentials, as such, here only this form of computer simulation is briefly introduced. Furthermore, there is a focus on molecular dynamics simulations and atomic geometry optimizations, which are the primary techniques used in this thesis.

Software

To date there exist numerous software packages that can be used to carry out molecular dynamics simulations. Certain packages, for example LAMMPS[11] and GROMACS[12–15], prioritize speed and performance by enabling simulations to be highly parallelized. In order to achieve these goals they often sacrifice flexibility and ease-of-use, not to mention the often feared compilation difficulties associated with these particular packages. As a result, users are limited to constructing their potentials with the pre-defined potential functions and using pre-defined auxiliary tools (thermostats, integrators, etc.). For potential development, users can port their own potential codes but this comes with the loss of any speed or performance boosts afforded by the simlation suite. Alternatively, users can turn to JIT compiled packages, for example

JaxMD[16] and Molly.jl[17], where flexibility and ease-of-use are not sacrificed for speed and performance. Unfortunately, these JIT compiled packages are fairly new and often do not offer the user or users the full range of features offered by other packages.

As a result, users that want a more flexible atomic simulation suite tend to turn to ASE[18]. However, ASE does not prioritize speed and performance, however, it provides interfaces to nearly all other software packages. This gives users a simple and flexible interface to perfroamnce focused packages, which cemented it as the defacto package for interacting with atomistic simulations. Modern programming languages, like Julia[19], offer the ability to develop software packages that can be as performant as LAMMPS or GROMACS while also being as flexible and intuitive as ASE. Allowing users to only depedend on a single package for all atomic simulation needs. However, building all the features and functionality available in ASE takes time and an active community of open-source developers.

Potentials

The interatomic potential describes the potential energy surface of the system being simulated. Hence, the accuracy of the simulations is directly tied to the sophistication and completeness of the empirical potential being used. For decades theoretical chemists have strived to develop realistic and transferrable water potentials. A potential is realistic when the simulations it is used for reproduce physical observations, while a transferrable potential is one that can reproduce observations not used in the development of the potential. For example, a potential developed using ice observations would be realistic if it reproduced observations for ice and transferrable if it reproduced observations for water.

The majority of the work on developing interatomic potentials has focused on water. Initial models were simple point charge (SPC) models, like SPC[20], SPC/E[21], and SPC-F[22]. These potentials represented the atoms as point charges with a nuetral molecular charge. Molecular bonds were often represented as harmonic potentials and intermolecular forces were O−O van der Waals forces plus electrostatic interactions from the point charges. At the time these models offered an incredibly powerful way to study water at the atomic scale. Shortly after, more sophisticated models began to be constructed; *ie.* TIP4P[23], TIP4P/2005[24], TIP4P/Ice[25], and TIP4P/2005f[26]. In an attempt to more accurately represent the electrostatic distribution around a water molecule, they add a fourth dummy atom along the bisector of the HOH angle. The total charge previously held by hydrogen atoms is now placed on the dummy atom, and the hydrogens are neutral. Furthermore, molecular bonds began to be represented by Morse potentials. This model was widely adopted by computational chemists and until this day is widely used in research studies due to its balance of accuracy and computational cost. However, these models lack transferrability and are often only able to accurately reproduce water under certain conditions. Attempting to overcome these limitations, models that accounted for many-body effects were constructed. Some examples of polarizable models are, TTMx-F[27–32], POLI2VS[33], AMOEBA[34–39], SCME/f[40–43], and MB-pol[44–47]. These water models have become the gold standard for atomistic simulations of water, in particular due to their high accuracy and transferrability.

1.2 Adsorption

Adsorption is the process by which molecules or atoms adhere to a surface, over time forming a thin film or layer. Figure 1.1 shows a simple schematic of the adsorption process, along with a schematic of the inverse process (desorption). Adsorption is a crucial step in many chemical and physical phenomena, including catalysis, atmospheric chemistry, and materials science. Adsorption can occur through various mechanisms, such as physisorption and chemisorption. The former is driven by weaker intermolecular forces, such as van der Waals or electrostatic interactions, while the latter involves the formation of chemical bonds between the adsorbate and the surface. Understanding the mechanisms and factors that influence adsorption is essential for controlling and optimizing various chemical and physical processes.

Astronomical modellers use reaction networks to model ice and gas molecular abundances in various interstellar environments and compare their results with observations.[48] These comparisons are used to validate the assumptions of chemical reactions that are occurring in the ISM. A vital part of these models is binding energies, the smallest amount of energy required to remove a molecule from a system of molecules (e.g., to desorb a molecule). The binding energies determine which type of molecules will be in the solid phase versus the gas phase in the ISM (where different possible reactions apply in each phase).[49] Experiments offer the most realistic value for the binding energy; however, they can only measure the statistical average binding energy. Recent models have shown this single value is insufficient, and binding energy distributions produce more realistic models.[50] Simulations can fill in the gaps by providing a complete distribution of the binding energies.[51,52]

Furthermore, in certain unique cases, binding energies cannot be measured experimentally due to physical limitations. For example, in the case of a molecule adsorbing

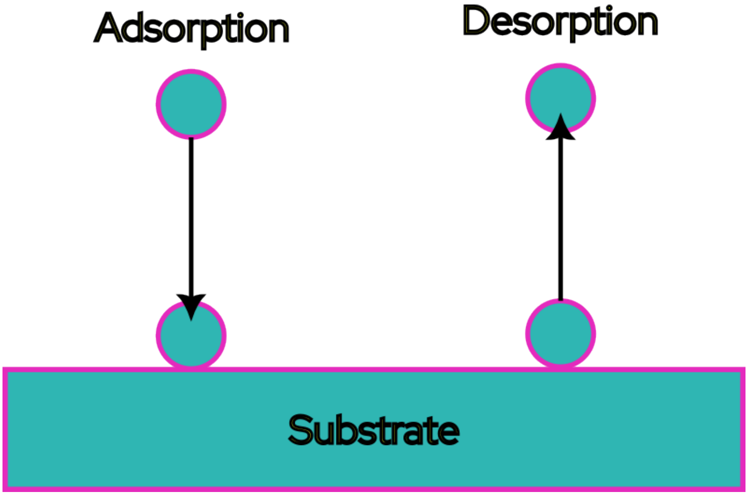

Figure 1.1: A simple representation of adsorption and desorption.

on a solid of the same species (e.g., H_2O on H_2O), any binding energy larger than the solid's cohesive energy will be impossible to measure because the temperature needed to desorb the admolecule (and thus measure the binding energy) is larger than the temperature needed to sublimate the surface to which the molecule is adsorbed. Again, here simulations are not limited by these constraints and can help shine light on the reality of the binding sites in question.

1.3 Vibrational Energy Relaxation

Figure 1.2 shows a simple schematic of the different types of normal modes for a gas-phase water molecule. 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[53], catalysis[54], and in the selectivity of chemical reactions[55]. 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. Understanding the mechanisms and factors that influence VER is essential for controlling and optimizing various chemical and physical processes.

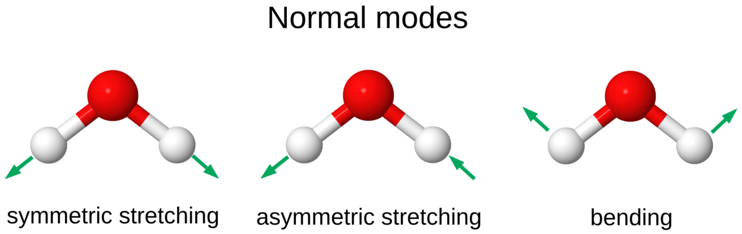

Figure 1.2: A simple explanation of the different types of normal modes for a water molecule.

In molecular simulations there is a number of ways to study VER. The most common way is to use non-equilibrium molecular dynamics (NEMD) simulations, where the molecule of interest is excited to a higher vibrational state, and the subsequent relaxation process is monitored over time. This approach can provide insights into the mechanisms, timescales, and relaxation pathways of the VER process. Frequently the results of these simulations are combined with experimental results, such as time-resolved pump-probe spectroscopy[56], to uncover the complex mechanisms involved in the VER process. However, NEMD studies are computationally challenging due to requirements on system size, integration time, and the need to average over an ensemble of simulation trajectories. In order to perform these studies, especially for long-lived vibrational modes, highly performant molecular dynamics software is necessary.

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. However, for water the inverse trend was observed, where the VER lifetime increased with increasing temperature.[57] The same study also reported that for ice, solid water, the VER lifetime was independent of temperature. The authors credit this to the strong anharmonicity of the hydrogen-bond mode in ice, which produces a strong coupling between the OH-stretch and hydrogen-bond modes. This results in the VER lifetime being weakly dependent on the thermal occupation of the vibrational modes of the surrounding molecules. For water, they were unable to determine the exact mechanism for the anomalous temperature dependence of the VER lifetime.

Deàk *et al.*[58] performed NEMD simulations of the VER of HDO in D_2O, where they found that the OH-stretch decay generates substantial excitation of the bending modes in D_2O. Following on these findings, Lock and Bakker[59] revealed that the anomalous temperature dependence in water was due to a decrease in the overlap between the OH-stretch mode and the overtone of the H-O-H bending mode.

1.4 Aims and Scope

The most important questions addressed by this thesis are:

1. How can atomistic simulations be improved so they are both easy to use and highly performant?
2. What are the most important physicochemical properties involved in the adsorption of H_2O on the ice Ih (0001) surface?
3. What are the most important physicochemical properties involved in the adsorption of CO on solid CO?
4. What processes are involved in the vibrational relaxation of a CO molecule in solid CO?

Chapter 2: This chapter summarizes the theory and methodology used for the research in this thesis. It starts by briefly covering the force fields used in the subsequent chapters. Then, it summarizes commonly used methods used to calculate vibrational modes and density of states of molecular systems.

Chapter 3: This chapter gives an overview of the features implemented in a Julia-based atomistic simulation suite developed during this PhD. An emphasis is placed on the flexibility and ease-of-use of the simulation suite, with examples given to highlight how simple usage is. At the same time, the resulting simulations achieve remarkable computational efficiency.

Chapter 4: The physicochemical properties that govern the adsorption of H_2O on the ice Ih (0001) surface are broken down and analyzed.

Chaper 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.

Chapter 6: Through NEMD simulations the VER process for CO in amorphous and crystalline CO is studied. A novel method of analyzing the MD trajectories is utilized, and the importance of the energy gap is scrutinized.

1.5 Main Results

Chapter 3: An atomic simulation suite was developed using the Julia programming language, with a test suite and online documentation. This software package is easy to install and quick to learn, making it incredibly attractive to the scientific community. When compared to the popular Python-based alternative (ASE), this new package provides up to a 6x speedup. This speedup enables users to perform previously infeasible simulations.

Chapter 4: A plethora of strong binding sites (sites with binding energy larger than the cohesive energy) is found on ice Ih (0001) surfaces across various degrees of proton ordering. This challenges the previously accepted idea that highly ordered surfaces would not produce strong binding sites. Furthermore, a comprehensive analysis focusing on understanding what physicochemical properties are most important for binding is done. This analysis allows for the creation of a site descriptor that can be used to predict which sites will have stronger binding energies. This novel descriptor builds off of previous global surface descriptors but addresses the issue of local influence on the binding.

Chapter 5: 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 more narrow distribution ($650 - 800$ K) and is orientation dependent. The median values 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: A novel analysis technique for studying the frequency-gap dependence of the decay time constant was developed. Anharmonic coupling between an excited CO molecule and a different CO isotope results in vibrational energy relaxation that is faster when the excited molecule has a lower frequency than the accepting molecule. On the other hand, 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 physicochemical properties for VEP are well captured by the classical pair potentials used to simulate the VER of CO.

1.6 Outlook

The collection of works within this thesis not only present 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. Here I briefly describe the works that have built off the works in each chapter (where available), and also outline other future prospects to come from each chapter.

The work presented in Chapter 5 has already been used in multiple subsequent works from other groups. Bariosco *et al.*[60] used the binding energy distributions calculated in Chapter 5 to solve the puzzling question of gaseous methonal detections in cold ISM conditions. They explained this strange observation by reasoning that methonal formed by multiple hydrogenations of CO could have a binding energy distributions as large as those seen for CO on CO. The low-end of this distribution would then be sufficiently weak to allow for desorption, hence explaining the observations. Enrique-Romero and Lamberts[61] used multiple CO cluster structures produced during the studies in Chapter 5 to investigate the formation of hydrogen cyanide and isocyanide in interstellar ices. The large amount of weakly bound sites reported in Chapter 5 has been used in several studies to explain experimental observations of CO desorption induced by low-energy photons.[62,63] These experimental observations are generally used to explain the observed gas-phase CO abundaces in cold ISM conditions, where CO is not expected to thermally desorb. Additional future works yet to be carried out are incorporating the binding energy distribution reported in an astrochemical model that utilizes distributions rather than single binding energy values. This work could potentially explain abundaces in gas-phase CO or other COMs, since diffusion and desorption would be increase by the low-end of the binding energy distribution.

The results described in Chapter 6 have also been used in multiple subsequent works from other groups. This work was partly inspired by the work of Santos *et al.*[64], where infrared-induced CO desorption was experimentally observed. The results in Chapter 6 show no significant transfer of vibrational energy to rotational or translational, in contradiction to the experimental work. Subsequent experimental studies based on the results from Chapter 6 found that the desorption did not originate from CO vibrations but rather thermalization of CO molecules or the vibrational motion of other molecules (*ie.* H_2O).[63,65] Additionally, Tsuge *et al.*[66] used the long VER timescales calculated in the work described in Chapter 6 to explain the formation of C_3O_2 in their experiments. The long VER timescales gave vibrationally excited CO molecules sufficient time to react with CCO, where the excitation energy was sufficient to surmount the reaction barrier. Finally, future studies that may still come from the work in Chapter 6 are those that apply the novel analysis technique for studying VER on other systems. This method could be quite useful for studying the VER of systems with more distinct energy gaps between different vibrational modes.

1.A Bibliography

[1] Louis J Allamandola, Max P Bernstein, Scott A Sandford, and Robert L Walker. Evolution of interstellar ices. *Space Science Reviews*, 90(1):219–232, 1999.

[2] EL Gibb, DCB Whittet, ACA Boogert, and AGGM Tielens. Interstellar ice: the infrared space observatory legacy. *The Astrophysical Journal Supplement Series*, 151(1):35, 2004.

[3] AC Adwin Boogert, Perry A Gerakines, and Douglas CB Whittet. Observations of the icy universe. *Annual Review of Astronomy and Astrophysics*, 53(1):541–581, 2015.

[4] Simon CO Glover, Christoph Federrath, M-M Mac Low, and Ralf S Klessen. Modelling CO formation in the turbulent interstellar medium. *Monthly Notices of the Royal Astronomical Society*, 404(1):2–29, 2010.

[5] Carina Arasa, Marc C van Hemert, Ewine F van Dishoeck, and Geert-Jan Kroes. Molecular dynamics simulations of CO_2 formation in interstellar ices. *The Journal of Physical Chemistry A*, 117(32):7064–7074, 2013.

[6] RL Hudson and MH Moore. Laboratory studies of the formation of methanol and other organic molecules by water+ carbon monoxide radiolysis: Relevance to comets, icy satellites, and interstellar ices. *Icarus*, 140(2):451–461, 1999.

[7] Robin T Garrod and Tyler Pauly. On the formation of CO_2 and other interstellar ices. *The Astrophysical Journal*, 735(1):15, 2011.

[8] SA Corcelli and JC Tully. Vibrational energy pooling in CO on NaCl (100): Methods. *The Journal of Chemical Physics*, 116(18):8079–8092, 2002.

[9] SA Corcelli and JC Tully. Vibrational energy pooling in CO on NaCl (100): Simulation and isotope effects. *The Journal of Physical Chemistry A*, 106(45): 10849–10860, 2002.

[10] Jascha A Lau, Li Chen, Arnab Choudhury, Dirk Schwarzer, Varun B Verma, and Alec M Wodtke. Transporting and concentrating vibrational energy to promote isomerization. *Nature*, 589(7842):391–395, 2021.

[11] Aidan P Thompson, H Metin Aktulga, Richard Berger, Dan S Bolintineanu, W Michael Brown, Paul S Crozier, Pieter J In't Veld, Axel Kohlmeyer, Stan G Moore, Trung Dac Nguyen, *et al.* LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Computer Physics Communications*, 271:108171, 2022.

[12] David Van Der Spoel, Erik Lindahl, Berk Hess, Gerrit Groenhof, Alan E Mark, and Herman JC Berendsen. GROMACS: fast, flexible, and free. *Journal of Computational Chemistry*, 26(16):1701–1718, 2005.

[13] Erik Lindahl, Berk Hess, and David Van Der Spoel. GROMACS 3.0: a package for molecular simulation and trajectory analysis. *Molecular Modeling Annual*, 7 (8):306–317, 2001.

[14] Sander Pronk, Szilárd Páll, Roland Schulz, Per Larsson, Pär Bjelkmar, Rossen Apostolov, Michael R Shirts, Jeremy C Smith, Peter M Kasson, David Van Der Spoel, *et al.* GROMACS 4.5: a high-throughput and highly parallel open source molecular simulation toolkit. *Bioinformatics*, 29(7):845–854, 2013.

[15] Mark James Abraham, Teemu Murtola, Roland Schulz, Szilárd Páll, Jeremy C Smith, Berk Hess, and Erik Lindahl. GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. *SoftwareX*, 1:19–25, 2015.

[16] Samuel S. Schoenholz and Ekin D. Cubuk. JAX, M.D: A framework for differentiable physics, 2020.

1.A Bibliography

[17] Joe G Greener. Differentiable simulation to develop molecular dynamics force fields for disordered proteins. *Chemical Science*, 15:4897–4909, 2024.

[18] Ask Hjorth Larsen, Jens Jørgen Mortensen, Jakob Blomqvist, Ivano E Castelli, Rune Christensen, Marcin Dułak, Jesper Friis, Michael N Groves, Bjørk Hammer, Cory Hargus, *et al.* The atomic simulation environment—a Python library for working with atoms. *Journal of Physics: Condensed Matter*, 29(27):273002, 2017.

[19] Jeff Bezanson, Alan Edelman, Stefan Karpinski, and Viral B Shah. Julia: A fresh approach to numerical computing. *SIAM Review*, 59(1):65–98, 2017.

[20] Herman JC Berendsen, James PM Postma, Wilfred F van Gunsteren, and Jan Hermans. Interaction models for water in relation to protein hydration. In *Intermolecular forces: proceedings of the fourteenth Jerusalem symposium on quantum chemistry and biochemistry held in jerusalem, israel, april 13–16, 1981*, pages 331–342. Springer, 1981.

[21] Herman JC Berendsen, J-Raúl Grigera, and Tjerk P Straatsma. The missing term in effective pair potentials. *Journal of Physical Chemistry*, 91(24):6269–6271, 1987.

[22] Kahled Toukan and Aneesur Rahman. Molecular-dynamics study of atomic motions in water. *Physical Review B*, 31(5):2643, 1985.

[23] William L Jorgensen, Jayaraman Chandrasekhar, Jeffry D Madura, Roger W Impey, and Michael L Klein. Comparison of simple potential functions for simulating liquid water. *The Journal of Chemical Physics*, 79(2):926–935, 1983.

[24] Jose LF Abascal and Carlos Vega. A general purpose model for the condensed phases of water: TIP4P/2005. *The Journal of Chemical Physics*, 123(23), 2005.

[25] JLF Abascal, E Sanz, R García Fernández, and C Vega. A potential model for the study of ices and amorphous water: TIP4P/Ice. *The Journal of Chemical Physics*, 122(23), 2005.

[26] Miguel A González and José LF Abascal. A flexible model for water based on TIP4P/2005. *The Journal of Chemical Physics*, 135(22), 2011.

[27] Christian J Burnham and Sotiris S Xantheas. Development of transferable interaction models for water. III. Reparametrization of an all-atom polarizable rigid model (TTM2–R) from first principles. *The Journal of Chemical Physics*, 116(4): 1500–1510, 2002.

[28] Sotiris S Xantheas, Christian J Burnham, and Robert J Harrison. Development of transferable interaction models for water. II. Accurate energetics of the first few water clusters from first principles. *The Journal of Chemical Physics*, 116(4): 1493–1499, 2002.

[29] Christian J Burnham and Sotiris S Xantheas. Development of transferable interaction models for water. IV. A flexible, all-atom polarizable potential (TTM2-F) based on geometry dependent charges derived from an ab initio monomer dipole moment surface. *The Journal of Chemical Physics*, 116(12):5115–5124, 2002.

[30] George S Fanourgakis and Sotiris S Xantheas. The flexible, polarizable, thole-type interaction potential for water (TTM2-F) revisited. *The Journal of Physical Chemistry A*, 110(11):4100–4106, 2006.

[31] George S Fanourgakis and Sotiris S Xantheas. Development of transferable interaction potentials for water. V. Extension of the flexible, polarizable, Thole-type model potential (TTM3-F, v. 3.0) to describe the vibrational spectra of water clusters and liquid water. *The Journal of Chemical Physics*, 128(7), 2008.

[32] CJ Burnham, DJ Anick, PK Mankoo, and GF Reiter. The vibrational proton potential in bulk liquid water and ice. *The Journal of Chemical Physics*, 128(15), 2008.

[33] Taisuke Hasegawa and Yoshitaka Tanimura. A polarizable water model for intramolecular and intermolecular vibrational spectroscopies. *The Journal of Physical Chemistry B*, 115(18):5545–5553, 2011.

[34] Pengyu Ren and Jay W Ponder. Polarizable atomic multipole water model for molecular mechanics simulation. *The Journal of Physical Chemistry B*, 107(24): 5933–5947, 2003.

[35] Pengyu Ren and Jay W Ponder. Temperature and pressure dependence of the AMOEBA water model. *The Journal of Physical Chemistry B*, 108(35):13427–13437, 2004.

[36] Jay W Ponder, Chuanjie Wu, Pengyu Ren, Vijay S Pande, John D Chodera, Michael J Schnieders, Imran Haque, David L Mobley, Daniel S Lambrecht, Robert A DiStasio Jr, *et al.* Current status of the AMOEBA polarizable force field. *The Journal of Physical Chemistry B*, 114(8):2549–2564, 2010.

[37] Lee-Ping Wang, Teresa Head-Gordon, Jay W Ponder, Pengyu Ren, John D Chodera, Peter K Eastman, Todd J Martinez, and Vijay S Pande. Systematic improvement of a classical molecular model of water. *The Journal of Physical Chemistry B*, 117(34):9956–9972, 2013.

[38] Chengwen Liu, Jean-Philip Piquemal, and Pengyu Ren. AMOEBA+ classical potential for modeling molecular interactions. *Journal of Chemical Theory and Computation*, 15(7):4122–4139, 2019.

[39] Chengwen Liu, Jean-Philip Piquemal, and Pengyu Ren. Implementation of geometry-dependent charge flux into the polarizable AMOEBA+ potential. *The Journal of Physical Chemistry Letters*, 11(2):419–426, 2019.

[40] Enrique Ricardo Batista. *Development of a new water-water interaction potential and application to molecular processes in ice.* University of Washington, 1999.

[41] K. T. Wikfeldt, E. R. Batista, F. D. Vila, and H. Jónsson. A transferable H_2O interaction potential based on a single center multipole expansion: SCME. *Phys. Chem. Chem. Phys.*, 15:16542–16556, 2013.

[42] Elvar Orn Jonsson, Asmus Ougaard Dohn, and Hannes Jonsson. Polarizable embedding with a transferable H_2O potential function I: Formulation and tests on dimer. *Journal of Chemical Theory and Computation*, 15(12):6562–6577, 2019.

[43] Elvar Orn Jonsson, Soroush Rasti, Marta Galynska, Jorg Meyer, and Hannes Jónsson. Transferable potential function for flexible H_2O molecules based on the single-center multipole expansion. *Journal of Chemical Theory and Computation*, 18(12):7528–7543, 2022.

[44] Volodymyr Babin, Claude Leforestier, and Francesco Paesani. Development of a “first principles” water potential with flexible monomers: Dimer potential energy surface, VRT spectrum, and second virial coefficient. *Journal of Chemical Theory and Computation*, 9(12):5395–5403, 2013.

[45] Volodymyr Babin, Gregory R Medders, and Francesco Paesani. Development of a “first principles” water potential with flexible monomers. II: Trimer potential energy surface, third virial coefficient, and small clusters. *Journal of Chemical Theory and Computation*, 10(4):1599–1607, 2014.

[46] Gregory R Medders, Volodymyr Babin, and Francesco Paesani. Development of a “first-principles” water potential with flexible monomers. III. Liquid phase properties. *Journal of Chemical Theory and Computation*, 10(8):2906–2910, 2014.

[47] Francesco Paesani. Getting the right answers for the right reasons: Toward predictive molecular simulations of water with many-body potential energy functions. *Accounts of Chemical Research*, 49(9):1844–1851, 2016.

[48] Jes K Jørgensen, Arnaud Belloche, and Robin T Garrod. Astrochemistry during the formation of stars. *Annual Review of Astronomy and Astrophysics*, 58(1): 727–778, 2020.

[49] EM Penteado, C Walsh, and HM Cuppen. Sensitivity analysis of grain surface chemistry to binding energies of ice species. *The Astrophysical Journal*, 844(1): 71, 2017.

[50] Kenji Furuya. A framework for incorporating binding energy distribution in gas-ice astrochemical models. *The Astrophysical Journal*, 974(1):115, 2024.

[51] Valentine Wakelam, J-C Loison, R Mereau, and M Ruaud. Binding energies: New values and impact on the efficiency of chemical desorption. *Molecular Astrophysics*, 6:22–35, 2017.

[52] Stefano Ferrero, Lorenzo Zamirri, Cecilia Ceccarelli, Arezu Witzel, Albert Rimola, and Piero Ugliengo. Binding energies of interstellar molecules on crystalline and amorphous models of water ice by ab initio calculations. *The Astrophysical Journal*, 904(1):11, 2020.

[53] Hiroshi Fujisaki and John E Straub. Vibrational energy relaxation in proteins. *Proceedings of the National Academy of Sciences*, 102(19):6726–6731, 2005.

[54] VP Zhdanov and KI Zamaraev. Vibrational relaxation of adsorbed molecules. Mechanisms and manifestations in chemical reactions on solid surfaces. *Catalysis Reviews*, 24(3):373–413, 1982.

[55] José I Pascual, Nicolas Lorente, Zhen Song, Horst Conrad, and H-P Rust. Selectivity in vibrationally mediated single-molecule chemistry. *Nature*, 423(6939): 525–528, 2003.

[56] Sander Woutersen and Huib J Bakker. Resonant intermolecular transfer of vibrational energy in liquid water. *Nature*, 402(6761):507–509, 1999.

1.A Bibliography

[57] Sander Woutersen, Uli Emmerichs, Han-Kwang Nienhuys, and Huib J Bakker. Anomalous temperature dependence of vibrational lifetimes in water and ice. *Physical Review Letters*, 81(5):1106, 1998.

[58] John C Deàk, Stuart T Rhea, Lawrence K Iwaki, and Dana D Dlott. Vibrational energy relaxation and spectral diffusion in water and deuterated water. *The Journal of Physical Chemistry A*, 104(21):4866–4875, 2000.

[59] AJ Lock and HJ Bakker. Temperature dependence of vibrational relaxation in liquid H_2O. *The Journal of Chemical Physics*, 117(4):1708–1713, 2002.

[60] Vittorio Bariosco, Lorenzo Tinacci, Stefano Pantaleone, Cecilia Ceccarelli, Albert Rimola, and Piero Ugliengo. Gaseous methanol in cold environments: is thermal desorption from low binding energy sites the explanation? *Monthly Notices of the Royal Astronomical Society*, 539(1):82–94, 2025.

[61] Joan Enrique-Romero and Thanja Lamberts. The complex (organic) puzzle of the formation of hydrogen cyanide and isocyanide on interstellar ice analogues. *The Journal of Physical Chemistry Letters*, 15(30):7799–7805, 2024.

[62] Antoine B Hacquard, Romain Basalgète, Samuel Del Fré, Jozef Rakovskỳ, Alejandro Rivero Santamaria, Ferdinand Benoit, Xavier Michaut, Géraldine Féraud, Mathieu Bertin, Maurice Monnerville, *et al.* Photodesorption of CO ices: Rotational and translational energy distributions. *The Journal of Chemical Physics*, 161(18), 2024.

[63] Laura Slumstrup, John D Thrower, Johanna GM Schrauwen, Thanja Lamberts, Emily R Ingman, Domantas Laurinavicius, Jessalyn DeVine, Jeroen Terwisscha van Scheltinga, Julia C Santos, Jennifer A Noble, *et al.* IR-induced CO photodesorption from pure CO ice and CO on amorphous solid water. *ACS Earth and Space Chemistry*, 2025.

[64] JC Santos, K-J Chuang, JGM Schrauwen, A Traspas Muiña, J Zhang, HM Cuppen, B Redlich, H Linnartz, and S Ioppolo. Resonant infrared irradiation of CO and CH_3OH interstellar ices. *Astronomy & Astrophysics*, 672:A112, 2023.

[65] L Slumstrup, JD Thrower, AT Hopkinson, G Wenzel, R Jaganathan, JGM Schrauwen, B Redlich, S Ioppolo, and L Hornekær. CO desorption from interstellar icy grains induced by IR excitation of superhydrogenated PAHs. *arXiv preprint arXiv:2507.07896*, 2025.

[66] Masashi Tsuge, Germán Molpeceres, Ryota Ichimura, Hideko Nomura, Kenji Furuya, and Naoki Watanabe. Formation of unsaturated carbon chains through carbon chemisorption on solid CO. *arXiv preprint arXiv:2509.16978*, 2025.

1.7 Bibliography