

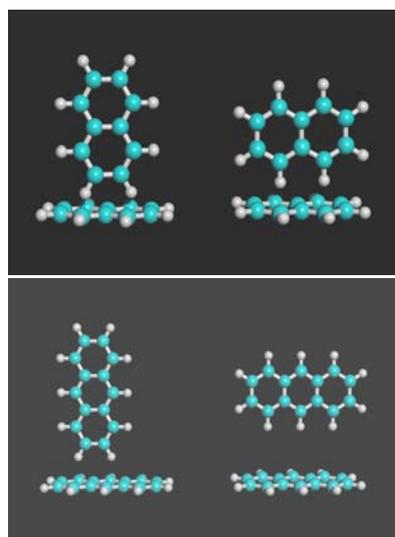
## Theory of Non-Bonded Interactions: Molecular Association and Assembly

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Long-range inter-molecular forces play important roles in many chemical and biological systems. They control, among others, the base-base interactions leading to the double helical structure of DNA, the function of the special pair in photosynthetic reaction centers, the packing of aromatic crystals, the formation of aggregates, the conformational preferences of polyaromatic macrocycles and chain molecules, as well important bulk fluid properties. It has also been found that weak interactions can be important in atmospheric chemistry. For example, the molecule ClOO (chloroperoxyl radical, formed by the collisions of the chlorine atoms with oxygen molecules) is critical in the catalytic, homogeneous destruction of ozone in the stratosphere. Most Cl-O<sub>2</sub> collisions lead to excited states of ClOO and we have found that many of these excited states surprisingly support weakly bound but stable van der Waals (vdW) complexes that must be considered to accurately predict the rates of ozone destruction.

The molecular systems ideally suited for a detailed study of the intermolecular potentials are vdW dimers and higher clusters of aromatic hydrocarbons formed as a direct consequence of intermolecular interactions. Given the maturity reached by quantum chemistry and the improvement in the algorithms used in quantum chemical calculations, it is logical to expect that highly correlated *ab initio* electronic structure methodologies could be a valuable tool to predict the structures and energetics of these clusters. We must assess the validity of these methodologies in the case of larger clusters of different aromatic molecules and possibly determine if alternative methodologies that incur lower computational expenses can be devised for these larger systems. Once the reliability and accuracy of these theoretical models are properly validated for gas-phase clusters they can be used for the generation of efficient and reliable empirical force-fields to be used in large-scale simulations of molecular systems in condensed phase such as liquids. This task, of course, also requires robust and efficient simulation methods that predict the different physical properties of bulk fluids in a reliable manner.

*Fundamentals of van der Waals Interactions in Aromatic Clusters.* The first phase of the project consisted of the use of second order Møeller-Plesset perturbation theory, MP2, with different basis sets in order to optimize the geometries and compute the relative binding energies of the lowest energy conformers for the dimers, trimers, and tetramers of benzene, naphthalene, and anthracene. These systems are a prototype for vdW clusters containing large aromatic molecules dominated by a delicate balance between electrostatic and dispersion forces. They were chosen on the basis of the availability of reliable experimental data. Overall, the results obtained in this project indicate that the combination of molecular dynamics simulations using the MM3 force field, followed by full geometry optimizations at the MP2/6-31G level of theory appear to provide a reliable tool for the study of vdW aromatic clusters. One significant outcome of this research has been the realization that the use of a small basis sets such as 6-31G with the *ab initio* MP2 methodology predicts binding energies closer to the experimental results than the corresponding binding energies computed with larger basis sets. This surprising result is very important given that calculations of vdW clusters with larger basis sets are highly prohibitive due to the computational resources needed.



Careful analysis of the data led to the conclusion that the source for this interesting behavior is rooted at a fortuitous but systematic cancellation of errors between the lack of convergence of the perturbation method MP2 and deficiencies in the 6-31G basis set. Given that the study of larger vdW clusters involving more than four aromatic molecules is almost impossible even at the MP2/6-31G level, we have performed a systematic comparison of the results obtained with the very efficient methodology Hartree-Fock Dispersion (HFD) previously developed in our group and the results computed at the MP2/6-31G level of theory. It was found that HFD predicts structures (see figures) and binding energies in very good agreement with the MP2/6-31G results.

Figure shows computed structures of (C<sub>10</sub>H<sub>8</sub>)<sub>2</sub> and (C<sub>14</sub>H<sub>10</sub>)<sub>2</sub>  
With details in recent publication:  
C. Gonzalez, E. Lim, "Evaluation HFD model as a practical tool for probing intermolecular potentials of small aromatic clusters: Comparison of the HFD and MP2 intermolecular Potentials", J. Phys. Chem. A 107, (2003).

**The CSTL-led research team develops and validates efficient theoretical and computational methodologies for the description of long-range interactions in gas-phase and solution to enable prediction of thermodynamic and transport properties of fluids.**

*Prediction of Mixture Phase Behavior Using Transition-Matrix Monte Carlo Simulation.* The fluid-phase behavior of mixtures is a subject of immense industrial and technical importance. For example, in multi-component systems, it is the fact that different coexisting phases often have different chemical compositions that serves as the basis for fundamental unit operations, such as absorption, distillation, and liquid extraction. Thus, knowledge of the phase coexistence properties of mixtures is crucial to the design of effective separation processes. Because laboratory determination of mixture phase equilibria can be potentially expensive and time-consuming, it is highly desirable to have a computational means for this purpose. While molecular simulation is ideally suited for this, only within the last twenty years have advances in simulation methodologies made this goal a realistic one. Current state-of-the-art simulation methods directly simulate phase coexistence and only yield a single equilibrium point per simulation. Therefore, a large number of these simulations are required to obtain phase equilibria data over a range of thermodynamic conditions, which can take a substantial amount of time.

Building upon recently developed transition-matrix Monte Carlo methods, we have developed a new simulation methodology capable of precisely predicting an entire isothermal fluid-phase diagram in a single simulation in a significantly shorter amount of CPU time relative to existing methods. To validate the mixture transition-matrix Monte Carlo method (M-TMMC), we have investigated a number of binary mixtures whose phase behavior is well known, and also mixtures that are known to pose problems for conventional methods. M-TMMC produced results in excellent agreement with literature data in all cases. Additionally, we found that the relative uncertainties of the predictions were at most 0.2%, an order of magnitude improvement over current methods. Because the method determines the system's free energy as a function of density and composition, the utility of the information yielded by this approach goes far beyond that for use in determining phase equilibria, and it should therefore serve as a highly efficient computational tool for studying a wide range of phenomena at the molecular level.

**The research team is extending this work in order to study vdW interactions between polar molecules, where dispersion forces and electrostatics interactions might be competitive with other forces such as hydrogen bonding. In addition, our HFD method will be used to probe the dynamics of cluster formation by means of Carr-Parinello simulations.**