Improved sampling in Monte Carlo simulations of small clusters

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In this thesis, improved sampling algorithms are applied to atomic and molecular clusters. The parallel-tempering Monte Carlo procedure is used to characterize the $(CO_2)_n$, n = 6, 8, 13, 19, and 38, clusters. The heat capacity curves of the n = 13 and 19 clusters are found to have pronounced peaks that can be associated with cluster melting. In addition, there is evidence of a low temperature "solid $\leftrightarrow$ solid" transition in the case of $(CO_2)_{19}$. The low-energy minima and rearrangement pathways are determined and used to examine the complexity of the potential energy surfaces of the clusters.

An algorithm combining the Tsallis generalized ensemble and the parallel tempering algorithm is introduced and applied to a 1D model potential and to Ar_{38}. The convergence of parallel tempering Monte Carlo simulations of the 38-atom Lennard-Jones cluster starting from the O_h global minimum and from the C_{5v} second lowest-energy minimum is also investigated. It is found that achieving convergence is appreciably more difficult, particularly at temperatures in the vicinity of the $O_h \rightarrow C_{5v}$ transformation, when starting from the C_{5v} structure. Compared to PTMC, the hybrid algorithm is about 10 times faster for reaching equilibrium in the 1D model potential and is about 3 times faster for reaching equilibrium in the LJ_{38} system when starting from the

second lowest energy minimum. The Wang-Landau free random walk algorithm is also applied to Ar_{13} and Ar_{38}.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

x

PREFACE

First and foremost, I would like to thank my advisor Ken Jordan with my deepest gratitude. He guided me into the wonderful area of computational chemistry. He is always there to help when I have difficulties in my research. Besides his comprehensive knowledge in chemistry, his zeal for science, work ethic, patience and life attitude impressed me a lot. He serves as my role model of a scientist and an educator.

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I want to thank my family, whose constant love and understanding supports me during the past five years. I thank my husband Kai Deng for his encouraging and love. I thank my parents, my sister Hantao and her family for their unconditional love and help. I would not be able to obtain this degree without my family's support. I am proud to be the Mom of my son David Deng. He was born and grew up with me during my PhD study at Pittsburgh. He is a great gift from God. I would like to thank God for everything.

1. Chapter 1 Introduction

1.1. The Monte Carlo method

Monte Carlo simulation methods are used routinely in many fields, including chemistry, biology, physics, engineering, and economics. The name "Monte Carlo" was coined by Metropolis (inspired by Ulam's interest in poker) during the Manhattan Project of World War II at Los Alamos[1,2].

The basic idea in Monte Carlo simulations is to simulate the random fluctuation of a system from state to state. In a Monte Carlo simulation, we directly simulate this process, creating a model on our computer and making it pass through a sequence of states in such a way that the probability of being in any particular state u at a given time t is equal to the weight $W_u(t)$ which that state would have in a real system. The advantage of the Monte Carlo approach in statistical mechanics is that we only need to sample a small fraction of the states of the system in order to obtain accurate estimates of the partition function. [3-5]

1.2. Statistical Mechanics of equilibrium systems[5]

1.2.1. Master equation and equilibrium state

Suppose that $P(\mu \to v)$ is the rate of the transition from state μ to state v, and $\omega_\mu(t)$ represents the probability that the system will be in state μ at time t. Then the master equation for the evolution of $\omega_\mu(t)$ in terms of the rates $P(\mu \to v)$ can be written as:

$$\frac{d\omega_\mu}{dt} = \sum_v [\omega_v(t)P(v \to \mu) - \omega_\mu(t)P(\mu \to v)]. \qquad (1.1)$$

The first term on the right-hand side of this equation represents the rate of transitions into state μ, and the second term represents the rate of transitions out of state μ. The probabilities $\omega_\mu(t)$ obey the sum rule

$$\sum_\mu \omega_\mu(t) = 1.$$ (1.2)

If the system reaches equilibrium, then $\dfrac{d\omega_\mu}{dt} = 0$, and the weights of all states become constant.

Gibbs showed that for a system in thermal equilibrium with a reservoir at temperature T, the equilibrium occupation probabilities are

$$p_\mu = \frac{1}{Z} e^{-\beta E_\mu},$$ (1.3)

where β denotes *1/kT*, k is the Boltzmann constant and Z is the partition function. For an equilibrium state, the probability distribution is known as the Boltzmann distribution.

From Equation 1.3, the expectation of an observable Q for a system in equilibrium is

$$\langle Q \rangle = \frac{1}{Z} \sum_\mu Q_\mu e^{-\beta E_\mu}.$$ (1.4)

Based on Equation 1.4, the internal energy, heat capacity, entropy, and Helmholtz free energy, F, of the system can be expressed

$$U = \frac{1}{Z} \sum_\mu E_\mu e^{-\beta E_\mu} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta},$$ (1.5)

$$C = \frac{\partial U}{\partial T} = -k\beta^2 \frac{\partial U}{\partial \beta} = k\beta^2 \frac{\partial^2 \log Z}{\partial \beta^2},$$ (1.6)

$$S = -k\beta \frac{\partial \log Z}{\partial \beta} + k \log Z,$$ (1.7)

and

$$F = U - TS = -kT \log Z \ . \tag{1.8}$$

In performing Monte Carlo simulations, one often calculates the quantities of interest directly without first evaluating the partition function.

1.2.2.   Fluctuations of energy in Monte Carlo simulations

For studies of phase changes, it is useful to calculate the energy fluctuations, which are given by

$$\left\langle (E - \langle E \rangle)^2 \right\rangle = \left\langle E^2 \right\rangle - \langle E \rangle^2 \ , \tag{1.9}$$

since

$$\left\langle E^2 \right\rangle = \frac{1}{Z} \sum_{\mu} E_{\mu}^{\ 2} e^{-\beta E_{\mu}} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \ . \tag{1.10}$$

Combining Equations 1.6 and 1.9, we get

$$\left\langle E^2 \right\rangle - \langle E \rangle^2 = \frac{C}{k\beta^2} \ . \tag{1.11}$$

This shows that the heat capacity is proportional to the energy fluctuations of the equilibrium system.

1.3. Principles of Monte Carlo simulations and the Metropolis algorithm

The Monte Carlo method in statistical mechanics generally uses Markov chains to sample a state (or configuration) C with a probability P(C) to replace multivariate integrations

$$\langle f \rangle = \sum_{C} f(C)P(C) \tag{1.12}$$

by simple averages

$$\langle f \rangle \cong \frac{1}{M} \sum_{i=1}^{M} f(C_i) \ .$$

(1.13)

It is very important to generate an appropriate random set of states according to the Boltzmann probability. In a Markov process, given a system in one state μ, the probability of accept moves from state μ to v is only based on the state μ. Almost all Monte Carlo schemes rely on Markov processes for generating the set of states used, since it is impossible to choose states at random and accept or reject them with a probability proportional to $e^{-\beta E_\mu}$, which would end up rejecting almost all states because the probabilities for their acceptance would be exponentially small.

Detail balance condition ensures that the Boltzmann probability distribution is achieved when the system has come to equilibrium. The condition for detailed balance is

$$p_\mu P(\mu \to v) = p_v P(v \to \mu) \ .$$

(1.14)

where p_μ is the probability of the system at state in equilibrium and $P(\mu \to v)$ is the transition probability for state μ to state v.

Detailed balance implies that on average the probability for the system going from μ to v should be the same as from v to μ. In this case the transition probabilities should satisfy

$$\frac{P(\mu \to v)}{P(v \to \mu)} = \frac{p_v}{p_\mu} = e^{-\beta(E_v - E_\mu)} \ ,$$

(1.15)

as well as the constraint

$$\sum_v P(\mu \to v) = 1 \ .$$

(1.16)

The Metropolis Monte Carlo algorithm, introduced by Nicolas Metropolis and his co-workers in 1953[6], is the most famous and widely used Monte Carlo algorithm.

Metropolis Monte Carlo follows equations 1.15 and 1.16. The transition probability P ($\mu \rightarrow v$) can be broken into two parts:

$$P(\mu \rightarrow v) = g(\mu \rightarrow v)A(\mu \rightarrow v) \ , \tag{1.17}$$

where $g(u \rightarrow v)$ is the selection probability, and $A(u \rightarrow v)$ is the acceptance ratio. In the Metropolis Monte Carlo algorithm, the selection probability $g(u \rightarrow v) = g(v \rightarrow u)$, so the detailed balance equation can be written as

$$\frac{P(\mu \rightarrow v)}{P(v \rightarrow \mu)} = \frac{g(\mu \rightarrow v)A(\mu \rightarrow v)}{g(v \rightarrow \mu)A(v \rightarrow \mu)} = \frac{A(\mu \rightarrow v)}{A(v \rightarrow \mu)} = e^{-\beta(E_v - E_\mu)} \ . \tag{1.18}$$

Metropolis Monte Carlo chooses the acceptance ratio as:

$$A(\mu \rightarrow v) = \min(e^{-\beta(E_v - E_\mu)}, 1) \ , \tag{1.19}$$

This means that if the new state (or new configuration) has a lower energy, it will always be accepted, and if it has higher energy than the old state (or configuration), it will be accepted based on the probability of $e^{-\beta(E_v - E_\mu)}$. The Metropolis algorithm satisfies the condition of detailed balance in Eq. 1.15 and the constraint condition of Eq. 1.16. Averages of the properties of interest are obtained by averaging over the sampled configurations. In order to obtain the value of a property such as energy E as a function of T, the simulation is repeated for a range of temperatures.

The Metropolis sampling technique has been successfully applied to study the equilibrium properties of liquids and polymers and to investigate protein folding. However, if there are high-energy barriers between the potential energy minima in a system, then Metropolis Monte Carlo simulations may become trapped in low energy minima regions and fail to reach equilibrium.

1.4. Problem of quasi-ergodicity and advanced Monte Carlo algorithms

The condition of ergodicity is the requirement that it should be possible for the Markov process to reach any state of the system from any other state, if the simulation is run long enough. As mentioned above, Metropolis Monte Carlo simulations may fail to reach equilibrium because of the existence of high energy barriers. The simulations then will not properly sample the potential energy surface and will give results which are incorrect. Such a simulation is often referred to as quasi-ergodic.[7] A variety of methods have been suggested for tackling this problem.

These approaches can be classified into two groups. The first group modifies the Boltzmann weight factor. Sampling using non-Boltzmann weight factors allows the simulation to overcome energy barrier and to sample much wider regions of phase space than by conventional methods.[8,9] The most well-known generalized-ensemble methods include umbrella sampling,[10-14] the multicanonical algorithm,[15-24] and Tsallis generalized thermostatistics.[25-28] Umbrella sampling was the first generalized ensemble method. Multicanonical Monte Carlo simulations perform random walks in a energy-phase space. The second group of methods takes advantage of ergodicity present at higher temperatures by allowing the exchange of configurations between low and high temperatures. By exchanging states at different temperatures, the higher-temperature simulations can thus "help" the lower-temperature ones cross the energy barriers between different basins. Jump walk[29-33] and parallel tempering Monte Carlo[34-37] are examples of this second group of algorithms.

1.4.1. Jump walking and parallel tempering Monte Carlo algorithm

The jump walking algorithm was first introduced by Frantz *et al.*[30] In this approach, a low-temperature simulation is permitted to attempt jumps to configurations

that were sampled in a simulation that was run at a higher temperature. A Metropolis criterion is applied when deciding whether or not to accept the move. To implement the jump walk algorithm, one usually first performs a high-temperature simulation and stores a subset of configurations from the high-temperature simulation. Then a low-temperature simulation reads the stored configurations and randomly picks one for the jump. This approach obviously requires large disk space to save the high temperature configurations.

The parallel tempering algorithm[34,35] is similar to the jump walking algorithm. In the parallel-tempering Monte Carlo procedure one performs in parallel Monte Carlo simulations at N different temperatures. Configurations from the simulations at adjacent temperatures are exchanged from time to time. The parallel tempering algorithm uses the ergodicty achieved at high temperature to help the simulations at low temperatures reach equilibrium. Since configuration generation and exchange are on the fly; thus the algorithm avoids hard disk storage space which speeds up the simulation. Better sampling of phase space is achieved than the jump walking algorithim. Figure 1.1 depicts schematically the parallel tempering Monte Carlo procedure. The parallel tempering (also called replica exchange) algorithm has been found to be a very powerful sampling algorithm[38-53] and it can overcome the quasi erogidicty problem caused by multiple-minima and high energy barriers between the minima. The parallel tempering algorithm has been widely used in many fields recently and has been used in combination with molecular dynamics simulations.

1.4.2.   Multicanonical Monte Carlo algorithm

The multicanonical MC (MUCA) method was developed by Bergs[15] and first applied to lattice spin models. The MUCA ensemble is based on a probability function in

which different energies are equally probable. The conventional Boltzmann weight is replaced by a non-Boltzmann weight, w_{NB}, which gives a flat energy distribution. As shown below,

$$P_{mu}(E) \propto g(E)W_{mu}(E) \equiv \text{constant} . \tag{1.20}$$

The flat distribution implies that a free random walk in the potential energy space is realized in this ensemble. This allows the simulation to escape from local minima and to sample the configurational space much more widely than the conventional canonical MC.

From the definition in Equation 1.20, the multicanonical weight factor is inversely proportional to the density of states, and can be written as:

$$W_{mu}(E) \equiv e^{-\beta_0 E_{mu}(E;T)} = \frac{1}{g(E)} . \tag{1.21}$$

Thus,

$$E_{mu}(E;T) = k_B T_0 \ln g(E) = T_0 S(E) . \tag{1.22}$$

Here, S(E) is the entropy in the multicanonical ensemble. Since the density of states of the system is usually unknown, the multicanonical weight factor has to be determined numerically before the simulation starts. This is a nontrivial task.

After the optimal multicanonical weight factor is determined, a multicanonical Monte Carlo simulation is performed with the usual Metropolis criterion; the transition probability of state x with potential energy E' is given by

$$w(x \to x') = \min(1, e^{-\beta_0 \Delta E_{mu}}) , \tag{1.23}$$

where

$$\Delta E_{mu} \equiv E_{mu}(E';T_0) - E_{mu}(E;T_0) . \tag{1.24}$$

Once the estimate of the density of states is obtained, the multicanonical weight factor can be directly determined by the formula below:

$$E_{mu}(E;T_0) = \begin{cases} \left.\dfrac{\partial E_{mu}(E;T_0)}{\partial E}\right|_{E=E_l}(E-E_l)+E_{mu}(E_l;T_0) \\ E_{mu}(E;T_0)=kT_0\ln g(E) \\ \left.\dfrac{\partial E_{mu}(E;T_0)}{\partial E}\right|_{E=E_H}(E-E_H)+E_{mu}(E_H;T_0) \end{cases} \qquad (1.25)$$

where $E_1 = \langle E \rangle_{T_1}$, and $E_H = \langle E \rangle_{T_H}$. The expectation value of a physical quantity A at any temperature T is then calculated from

$$\langle A \rangle_T = \frac{\sum\limits_E A(E)g(E)e^{-\beta E}}{\sum\limits_E g(E)e^{-\beta E}} \qquad (1.26)$$

It is a very difficult task to calculate density of states directly with high accuracy for large systems. Almost all the methods to generate density of states are based on an accumulation of the energy histogram. On the other hand, in a multicanonical simulation, the density of states need not be very accurate. The re-weighting procedure does not depend on the accuracy of the density of the states as long as the histogram can cover all important energy levels with sufficient statistics.

1.4.3. Tsallis statistics

Tsallis statistics avoids the problem presented by the need to predetermine the weight function in MUCA.[25]

The generalized thermostatistics proposed by Tsallis defines the generalized entropy as

$$S_q = k_B \frac{\int dr^N [1 - p_{Tsallis}(r^N)^{q-1}]p_{Tsallis}(r^N)}{q-1}, \qquad (1.27)$$

with the constraints

$$\int dr^N p_{Tsallis}(r^N) = 1, \text{ and } \int dr^N [p_{Tsallis}(r^N)]^q E(r^N) = \text{constant}, \qquad (1.28)$$

where q is a parameter greater than 1.

$$p_{Tsallis}(r^N) = \frac{1}{Z_q}[1 - (1-q)\beta E(r^N)]^{1/(1-q)}, \qquad (1.29)$$

where

$$Z_q = \int dr^N [(1 - (1-q)\beta E(r^N)]^{1/(1-q)}. \qquad (1.30)$$

When $q \rightarrow 1$, the Tsallis distribution becomes the Boltzman distribution.

The configurations are sampled with the distribution $[p_{Tsallis}(r^N)]^q$ using the effective energy

$$E_{eff} = \frac{q}{\beta(q-1)}\ln[1 - (1-q)\beta(E - E_0)], \qquad (1.31)$$

where E_0 is chosen so as to lie below the energy of the global minimum. When $q = 1$, the acceptance probability becomes equal to Metropolis Monte Carlo method. For $q < 1$, the energy distributions become narrower and more focused around minima, while for $q > 1$, they become broader and exhibit greater probability in barrier regions.

The acceptance ratio of the Tsallis generalized MC method is

$$P_{i \rightarrow j} = \min(1, e^{-\beta(E_{eff\,j} - E_{eff\,i})}) \qquad (1.32)$$

and the thermodynamic average of any physical quantity f can be calculated over a wide temperature range by

$$\langle f \rangle_T = \frac{\sum_E f \cdot w^{-1} \cdot e^{-\beta E}}{\sum_E w^{-1} \cdot e^{\beta E}} \tag{1.33}$$

1.4.4. Wang-Landau free random walk in energy space

The free random walk in energy space with a flat histogram[54,55] has become known as "Wang-Landau sampling". This algorithm is based on the observation that if one performs a random walk in energy space and the probability to visit a given energy level E is proportional to the reciprocal of the density of states $1/g(E)$, then a flat histogram is generated for the energy distribution.

The partition function can be written as a sum over all states or over all energies E,

$$Z = \sum_i e^{-\beta E_i} = \sum_E g(E)e^{-\beta E}, \tag{1.34}$$

where $g(E)$ is the density of states. Since $g(E)$ is independent of temperature, it can be used to find all properties of the system at different temperatures.

The idea of Wang-Laudau is very similar to multicanonical methods. An accurate knowledge of the weight factors used in multicanonical methods is equivalent to a knowledge of the density of states of the system. The Wang-Landau method directly and self-consistently determines the density of states by performing a random walk in the energy space, with a probability proportional to the reciprocal of the density of states. A convertion factor is defined at the beginning of the simulation, starting with a big number compared to 1. It will iteratively be updated when a flat energy histogram has been achieved during the simulation. When the convertion factor is close to 1, a reliable and accurate estimate of $g(E)$ will be obtained.

1.4.5. Other methods

11

There are many more new sampling methods in Monte Carlo simulation besides the four widely used algorithms described earlier. Hetenyi *et al.* introduced the multiple "time step" Monte Carlo by divided the potential into a short- and long-range part[56]; Berne *et al.* introduced catalytic Monte Carlo[57]; Brown *et al.* developed cool walking algorithm[58]; and Transition Matrix Monte Carlo method[59-61]. Thus far, the most popular methods using in sampling are parallel tempering Monte Carlo and multicanonical Monte Carlo.

1.5. The overview of the thesis and application of advanced sampling algorithms

The thesis is mainly focused on using the advanced sampling method to investigate weakly bound clusters. One of the reasons often stated for studying small weakly bound clusters is that they provide a bridge between micro-systems and bulk systems. Clusters can provide insights into the transformation from finite to bulk behavior. They can also exhibit properties that are different from both the properties of the individual atom or molecule and those of bulk matter.

In Chapter 2, the parallel tempering Monte Carlo procedure is applied to investigate CO_2 clusters. In spite of the importance of CO_2 as a solvent, relatively little is known about CO_2 clusters. Exceptions are the CO_2 dimer and trimer which have been the subject of several experimental and theoretical studies. We are especially intrigued by the thermodynamic properties, in particular the melting behavior, of CO_2 clusters and how this behavior depends on the details of the underlying potential energy surface.

In Chapter 3, a hybrid algorithm of parallel tempering Monte Carlo simulation and Tsallis statistics has been introduced and applied on a 1D model potential. The LJ_{38} cluster, which is known to have an extremely rugged potential energy surface has been

investigate using both parallel tempering Monte Carlo and the hybrid algorithm. The results show the when the simulation starting from the second minima, the simulations tend to very hard to reach equilibrium and it shows the potential to be a very good test system for new algorithm development. Comparing to PTMC, the hybrid algorithm is about 10 times faster for reaching equilibrium in the 1D model potential and is about 3 times faster for reaching equilibrium in the Ar_{38} system when starting from the second lowest energy minimum.

In Chapter 4, the Wang-Landau free random walk algorithm is used in simulation of Ar_{13} and Ar_{38}. The algorithm is found to work well for Ar_{13} which has a simple potential energy landscape. However, in the Ar_{38} system, difficulties are met in reaching a flat distribution because of the difficulty in generating configurations in the low-energy regions.

Appendix A is a separated project collaborated with professor Cohen. The research is focused on computational study of the stereochemistry of intramolecular carbolithiation of a secondary alkyllithium to produce a 2-substituted cyclopentylmethyllithium using DFT theory.

Appendix B is a project that I have involved. My major contribution for that project is using eigenmode following algorithm to locate the global minima of $(H_2O)_{21}$.

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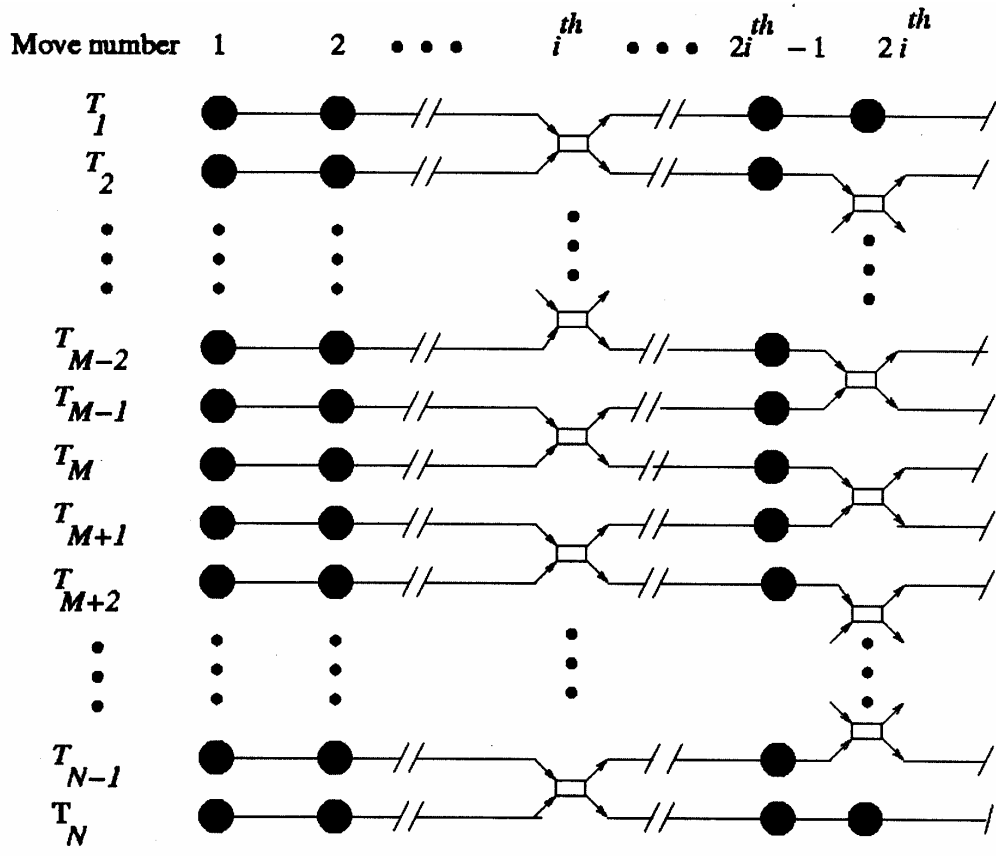
Figure 1.1 Schematic of the parallel tempering algorithm. Simulations at the *N* temperatures of interest, $T_1, T_2...T_N$ are carried out in parallel, one temperature per processor. In each simulation, most moves are carried out with the Metropolis algorithm, represented by the filled circles, and the remaining moves involve exchanges, represented by the unfilled rectangles, between the configurations at adjacent temperatures. The figure was adapted from Arnold Tharrington's thesis.

2. Chapter 2 Finite temperature properties of $(CO_2)_n$ clusters

2.1. Introduction

Carbon dioxide has attracted considerable experimental and theoretical attention both because of the importance of its supercritical state for chemical separations and because it is a prototype for molecules for which the dominant electrostatic interactions are quadrupole-quadrupole in nature.[62] Although the net dipole moment for CO_2 is zero, there is a clear charge separation in CO_2 molecule with the bond electron density being polarized more towards the oxygen atoms, leaving the carbon atom with a partial positive charge and the two oxygen atoms with partial negative charges. Because the molecular charge is very well characterized, CO_2 has attracted attention from the theorists. For example, the crystal structure, volume compression and vibrational properties of solid CO_2 have been calculated with various model potentials and compared with the experimental results.[63-65]

In spite of this, our knowledge of the properties of CO_2 clusters lags behind that for clusters of polar molecules such as water. Although several Monte Carlo and molecular dynamic simulations of $(CO_2)_n$ clusters have been carried out,[66-70] there remain unresolved issues including the connections between the thermodynamic behavior and the topology of the underlying potential energy surfaces. Also, it appears that some of these simulations failed to achieve equilibrium, particularly at the lowest temperatures considered.

In the present study the parallel-tempering Monte Carlo method,[71] which is well suited for achieving equilibrium in low-temperature simulations when there are large energy barriers separating low-lying local potential energy minima, is combined with long production cycles to calculate the finite-temperature behavior of $(CO_2)_n$, $n = 6, 8, 13,$

and 19, clusters. To aid in analyzing the nature of the transitions associated with peaks in the heat capacity curves, the populations of inherent structures are calculated as a function of temperature. Stillinger and Weber proposed the idea to partitioning the potential surface into basins of attractions[72]. The inherent structures of quenching provide insight into the accessible local minima of the potential energy surface for a temperature of simulation. Later, Becker and Karplus introduced disconnecitivity diagrams to represent the topology of the potential energy surface[73]. Those two methods are combined in our analysis to help describe the potential energy surface. For each simulation, the saved configurations are quenched (minimized) to their closed local minimum. For each cluster considered, the low-energy minima and transition states are located using the eigenmode-following method[74-76] and used to construct disconnectivity graphs to provide insight into the topology of the potential energy surface, in particular, the accessibility of different regions of configuration space as a function of energy. Simulations of $(CO_2)_{38}$ are also performed using parallel tempering Monte Carlo method.

2.2.Methodology

2.2.1. Model potential

The CO_2 - CO_2 interactions are described by a two-body model potential due to Murthy *et al.*[77] This is a rigid monomer model with CO bond lengths equal to the experimental (R_e) value and interactions between monomers described by electrostatic and 6-12 Lennard-Jones terms. The former are incorporated by means of five point charges on each monomer, the locations and values of which are given in Table 1. The Lennard - Jones terms are atom-atom in nature, with the parameters being given in Table 2.

The CO_2 molecule is set to be rigid and the potential between CO_2 atom i and CO_2 atom j can be written as:

$$U_{ij} = \sum U_{LJ} + \sum U_{elec}.$$

Table 2.1 Location of the point charges in the Murthy CO_2 potential

Site	Z(Å)	Q(e)
1	-1.5232	0.1216
2	-1.0663	-0.6418
3/C[b]	0	1.0404
4	1.0663	-0.6418
5	1.5232	0.1216

[a] From Ref. 77.

[b] The third point charge is located on the C atom.

Table 2.2 Lennard-Jones parameters for the Murthy CO_2 model potential[a]

Atom pair	ε(K)	σ(Å)
C-C	26.3	2.824
O-O	75.2	3.026
C-O	44.5	2.925

[a] From Ref. 77.

For $(CO_2)_2$ and $(CO_2)_3$ the Murthy potential gives structures and binding energies in good agreement with the results of experiment and MP2 calculations.[78,79] At first sight, the success of the Murthy potential for describing $(CO_2)_2$ and $(CO_2)_3$ is somewhat surprising since it does not include an explicit induction contribution, which has been shown by symmetry-adapted perturbation theory (SAPT) calculations to be important for

these clusters.[80] This suggests that either the LJ or the electrostatic term (or perhaps both) in the Murthy potential is too attractive, thereby "mimicking" the induction interactions. The use of enhanced electrostatic terms to incorporate induction is a common procedure, with a representative example being the TIP4P model for water.[81]

2.2.2. Parallel tempering Monte Carlo procedure

Monte Carlo simulations were carried out using the parallel tempering algorithm,[34,35] in which simulations over the range of temperatures of interest are carried out in parallel. The sets of configurations generated at the various temperatures are called "replicas". Most moves are "local", *i.e.*, confined to individual replicas, with trial moves translations or rotations of individual molecules, being accepted or rejected according to the Metropolis algorithm:

$$P_{i \to j} = \min\left\{ 1, \exp[-\beta(E_j - E_i)] \right\} , \tag{2.1}$$

where $P_{i \to j}$ is the probability for accepting a move from configuration "i" with energy E_i to configuration "j" with energy E_j, and β is related to the inverse temperature *via* $\beta = (kT)^{-1}$. In the implementation of the parallel tempering algorithm used in the present study, the local moves were carried out by attempting, in succession, translation and rotation of molecules selected at random. The maximum step sizes were chosen so as to maintain close to 50% acceptance ratios. The remaining moves involved attempted swaps of configurations between replicas at adjacent temperature. The acceptance probability for an attempted exchange of configurations from the T_i and T_{i+1} replicas is given by

$$P_{i \leftrightarrow i+1} = \min\left\{ 1, \exp[-(\beta_i - \beta_{i+1})(E_i - E_{i+1})] \right\} , \tag{2.2}$$

where $\beta_i = (kT_i)^{-1}$. Exchanges were attempted once every 100 moves, and were made only between replicas at adjacent temperatures. On odd swap cycles, the attempted exchanges were between the (T_1, T_2), (T_3, T_4), *etc.* replicas, and on even cycles, between the (T_2, T_3), (T_4, T_5), *etc.* replicas. Additional details on the parallel tempering code used to carry out the simulations are given in Ref. 82.

At the highest temperatures used in the simulations, evaporative events could occur, which would seriously impact convergence. This problem was avoided in the simulations on the three smaller clusters by rejecting moves that placed one or more of the molecules over a specified distance [6 Å for $(CO_2)_6$ and $(CO_2)_8$ and 8 Å for $(CO_2)_{13}$] from the center of mass of the cluster. For $(CO_2)_{19}$, moves that placed the C atom of an individual monomer more than 5 Å from the C atoms of all other monomers in the cluster were rejected. This constraint method is called "maximum group distance" method. The difference constraint method for $(CO_2)_{19}$ cluster allows the cluster having extended forms as well as compact forms.

One of the challenges in carrying out parallel-tempering Monte Carlo simulations is the choice of an appropriate grid of temperatures covering the temperature range of interest. The temperature range should encompass regions over which the structural transformations of interest occur. It is also essential that all important energy barriers are readily overcome at the highest temperature employed and that there is appreciable overlap between the potential energy distributions from the simulations at adjacent temperatures. In the present study, twenty temperatures spanning 20-150 K were used for $(CO_2)_n$, $n = 6, 8, 13$, and twenty-four temperatures spanning 20-200 K were used for $(CO_2)_{19}$. These temperature ranges were chosen on the basis of series of preliminary

parallel-tempering Monte Carlo simulations with different choices of the temperatures. Additional simulations, employing up to 28 temperatures, were also carried out, results obtained were very close to those from the simulations using fewer temperatures.

For each cluster studied, two parallel-tempering Monte Carlo simulations were carried out, one starting from a configuration chosen at random from a preliminary high-temperature Metropolis Monte-Carlo simulation, and the other starting from the global minimum structure. Comparison of the results of the two simulations provides a check on attainment of equilibrium. For each simulation, averaging was done over 2×10^7 moves following an equilibration period, which ranged from 10^7 moves for $(CO_2)_6$ and $(CO_2)_8$ to 2×10^7 moves for $(CO_2)_{13}$ and 3×10^7 moves for $(CO_2)_{19}$. The equilibration data are not counted on the average. Each standard Monte Carlo move includes a translation move of a random picked molecule and a rotational move a random picked molecule. The step size of each kind of moved are adjusted every 1000 moves in the equilibration period. The acceptance criterion for the translational and rotational moves was maintained 50% by adjusting the step size. During the simulation, the configurations are saved every 40000 moves for further analysis.

The heat capacity was calculated using

$$C_{N,V,T}(T) = \frac{\left\langle U^2 \right\rangle - \left\langle U \right\rangle^2}{RT^2},$$

(2.3)

where R is the gas constant.

For monitoring convergence of the simulations and for interpreting structural transformations, it is useful to examine the distributions of inherent structures, obtained by "quenching" configurations sampled in the simulations. In the present study, 500

configurations, chosen at equal intervals, were saved from each replica and optimized to their inherent structures by use of the eigenmode-following method as implemented in the Orient 4.3 program.[83]

2.2.3.   Disconnectivity graphs

Over the past few years much progress has been made in establishing the relationship between the topology of the potential energy surface and the difficulty of achieving equilibrium in finite temperature (or energy) simulations.[82,84,85] This requires locating the local potential energy minima and the transition states connecting the minima. In the present study, this was accomplished by carrying out eigenmode-following (EF)[74,76] searches in directions, both parallel and anti-parallel to specific eigenvectors of the Hessian, for each of the minima located in the course of the optimizations. Searches were done along the eigenvector associated with the lowest 8, 15, 24 and 50 eigenvalues for $(CO_2)_6$, $(CO_2)_8$, $(CO_2)_{13}$ and $(CO_2)_{19}$, respectively. For each transition state located in this manner, subsequent searches were carried out to identify the minima connected to the transition state, allowing construction of the rearrangement pathways. These results were used to construct disconnectivity graphs,[86] which show the minima that are accessible at different energy thresholds and thus provide a convenient visual representation of the connectivity/disconnectivity of different regions of the potential energy surface.[73,86]

2.3. Results

The heat capacity *vs.* temperature curves, obtained from the parallel-tempering simulations, are shown in Figure 2.1. For each cluster, curves from both the simulation started at the global minimum structure and that started from a randomly selected

structure are reported and found to be in excellent agreement, providing evidence that the calculations have achieved equilibrium. The heat capacity curves of $(CO_2)_6$ and $(CO_2)_8$ display broad, weak peaks centered near $T = 70$ K. In contrast, the heat capacity curves of $(CO_2)_{13}$ and $(CO_2)_{19}$ display pronounced, narrower peaks near $T = 90$ K. In analyzing these results, it is useful to examine the low-energy minima from the EF optimizations, the distributions of inherent structures sampled in the finite temperature simulations, and the disconnectivity graphs. The energies of the low-lying local minima of the various clusters are indicated in Figure 2.2. The analyses of the results for various clusters are presented below.

i) $(CO_2)_6$

The six lowest-energy minima of $(CO_2)_6$ obtained from the EF optimizations are shown in Figure 2.3. These isomers are very close in energy, being spread over only 0.57 kcal/mol. The global minimum, which can be viewed as two interacting cyclic trimers, is only 0.04 kcal/mol more stable than the second lowest-energy isomer with an octahedral-like structure, which, in turn, is only 0.28 kcal/mol stable than the next lowest-energy structure (see Fig. 2.2).

Figure 2.4 reports the distributions of inherent structures of $(CO_2)_6$ sampled in the T = 20, 55, 80, and 100 K replicas. In the $T = 20$ K replica, only the two lowest-energy inherent structures have significant population. The populations of these two isomers gradually decrease and those of the higher energy structures gradually grow in with increasing temperature. At $T = 55$ K, which corresponds to a weak, low-temperature shoulder on the broad peak on the heat capacity curve, the six lowest-energy structures account for about 70% of the inherent structure distribution. Even at $T = 100$ K, the two

lowest-energy structures together still account for about 9% of the population and the six lowest-energy structures for about 32% of the population. Although Etters *et al.*[2] concluded that $(CO_2)_6$ undergoes a melting transition near 70 K, in our opinion, the density of states near this temperature is not sufficiently high to attribute the broad, weak peak in the heat capacity curve to a melting transition.

The disconnectivity graph for $(CO_2)_6$ is shown in Figure 2.5. Overall, the diagram is quite simple, and the potential energy surface can be characterized as having a single funnel. There is a barrier of about 1 kcal/mol for interconversion of the two lowest energy isomers. Thus, it should be possible to achieve sizable populations of both these isomers in a seeded expansion.

ii) $(CO_2)_8$

The $(CO_2)_8$ cluster possesses a very large number of low-lying potential energy minima. In fact, we have identified 158 minima within 1 kcal/mol and 490 minima within 2 kcal/mol of the global minimum. These are considerably in excess of the number of local minima found for the $(CO_2)_6$, $(CO_2)_{13}$, and $(CO_2)_{19}$ clusters in the same energy ranges.

The six lowest-energy isomers of $(CO_2)_8$, fall within an energy range of 0.24 kcal/mol and are depicted in Fig. 2.6. The inherent structure distributions for $(CO_2)_8$ are reported in Fig. 2.7. For the $T = 20$ K replica, the global minimum structure is most populated (~73%), with about 20% of the remaining population being associated with the second lowest-energy isomer. In the $T = 50$ K replica, the population of the two lowest-energy isomers combined has dropped to 40%, with most of the remaining population being spread over a group of isomers with inherent structure energies ranging from -20.3

to -19.8 kcal/mol. In the $T = 80$ K replica, the net population of the two lowest-energy isomers has dropped to about 7%, with the remaining population being spread over a large number of isomers.

The disconnectivity graph for $(CO_2)_8$ is shown in Fig. 2.8. The potential energy surface of this cluster is characterized by two low-energy basins, each containing about 20 local minima. There is a barrier of about 1 kcal/mol between the lowest-energy structures in one basin to the lowest-energy structure in the other basin. Comparison of Figures 2.7 and 2.8 reveals that near $T = 70$ K the $(CO_2)_8$ cluster has an appreciable population of higher-energy structures associated with the two low-energy basins as well as of a large number of structures associated with other regions of the potential energy surface. While, the density of inherent structures is high enough to view the cluster as "liquid-like" for temperatures above about 80 K, this system does not possess a sizable energy gap between the global minimum or small group of low-energy minima and the remaining higher-lying minima (see Fig. 2.2), and it has been argued that such an energy gap is required for a cluster to display a well-defined melting transition.[87]   Due to the absence of the energy gap, the broad transition found for $(CO_2)_8$ can be viewed as "glass-like" rather than originating from a well-defined melting transition.

iii) $(CO_2)_{13}$

The structures of the six lowest-energy isomers of the $(CO_2)_{13}$ cluster are shown in Fig. 2.9. In agreement with Ref. 69, the global minimum has an icosahedral-like structure of S_6 symmetry. The global minimum is predicted to be 1.16 kcal/mol more stable than the second lowest-energy isomer, which belongs to a group of isomers with distorted icosahedral structures. This situation is analogous to that for the LJ_{13} cluster, for

which the global minimum is a highly stable icosahedral structure, followed in energy by a group of distorted-icosahedral isomers, and then by non-icosahedral structures.[88]

The inherent structure distributions of $(CO_2)_{13}$ are reported in Fig. 2.10. Only the global minimum structure has an appreciable population in the $T = 20$ K replica. Even at $T = 60$ K, it accounts for over 99% of the total population. However, at $T = 90$ K, the population of the global minimum structure has dropped to about 48%, with the remaining population being spread over a large number of higher-energy structures. At $T = 110$ K, the population of the global minimum structure has fallen to below 0.5%.

The inherent structure distributions and the large peak in the heat capacity curve of $(CO_2)_{13}$ are both indicative of a relatively sharp melting transition near 90 K. This is in agreement with Maillet *et al.*, who concluded on the basis of molecular dynamics simulations that the $(CO_2)_{13}$ cluster melts near $T = 95$ K. The disconnectivity graph for $(CO_2)_{13}$ shown in Fig. 2.11 displays a single-funnel topology similar to that found for LJ_{13}.

iv) $(CO_2)_{19}$

The geometries of the six lowest-energy isomers of $(CO_2)_{19}$ are shown in figure 2.12. All of these may be viewed as icosahedral-like with an approximately icosahedal $(CO_2)_{13}$ core and with the remaining six molecules forming a surface layer. These six isomers are close in energy, being spread over only 0.5 kcal/mol. The inherent structure distributions are plotted in figure 2.13. For the T = 20 K replica, about 87% of the population is associated with the global minimum, with the remaining population being due to the next two-lowest energy isomers. At $T = 50$ K, these three isomers still dominate, but now isomer **2**, is most populated at 38%. At $T = 80$ K, somewhat below the

25

temperature of the maximum in the large peak in the heat capacity curve, the net population of the three lowest energy isomers has fallen to about 8%, with the remaining population being distributed over a large number of higher-lying isomers. At $T = 100$ K, there is no significant population of the six lowest-energy isomers. The trends in the inherent structure distributions provide strong evidence that the large peak near 90 K in the heat capacity curve of $(CO_2)_{19}$ is due to a melting-like transition. This is consistent with the conclusion of Maillet *et al*., who reported, based on molecular dynamics simulations, that $(CO_2)_{19}$ melts near $T = 95$ K.

The heat capacity curve for $(CO_2)_{19}$ also displays a weak shoulder near $T = 50$ K. This is due to a "solid" to "solid" transition between isomer **1** and isomers **2** and **3**. This interpretation is supported by the disconnectivity graph of $(CO_2)_{19}$ shown in Fig. 14, which reveals that each of the three low-energy isomers is associated with a different basin. The barriers to go from the lowest-energy isomer to the basins containing isomers **2** and **3** are over 3 kcal/mol.

As we have mentioned before, the simulations of $(CO_2)_{19}$ were also carried out at 28 temperature replicas for comparation the convergence of the simulations and investigation of the influence of temperature spacing. 28 temperatures ranging from 20 – 150 K have been applied to the simulation. The temperature grids for those extra simulations are finer. Figure 2.15 shows the results of heat capacity curves running at different temperature grids. From Figure 2.15 we can see there is no distinguishable difference among the results of simulations with different temperature grids. The simulation using 24 temperatures spanning from 20 – 200 K is good and have enough overlap between the sampling distributions.

v) $(CO_2)_{38}$

The parallel tempering Monte Carlo algorithms are also applied to the simulation of $(CO_2)_{38}$ cluster. Two runs of simulations have been performed with different random start geometry and slightly different temperature spacings. 32 temperatures has been used from 20K to 200K. The heat capacity results are reported in figure 2.16. For each simulation, the average results are calculated over the production cycle of $4x10^7$ cycles, which following by the equilibrium cycles is around $4x10^7$ steps. Similar to the simulations of $(CO_2)_{19}$, the constraint method to prevent evaporation is so called "maximum group distance" method. Moves that placed the C atom of an individual monomer more than 8 Å from the C atoms of all other monomers in the cluster were rejected. It appears that the system has not reach equilibrium since the agreements in the heat capacity curves between the two runs are not very well. But both of them show the similar pattern with two peaks in the heat capacity curves. There is a broad peak around 100 K and an extra sharp big peak around 180 K. The broad peak about 100 K may be described as a solid-solid state transition. The sharp peak around 180 K may be described as the melting transition. The temperature of the sharp peak is in a fair good agreement with the sublimation temperature of dry ice which is 194.5 K.

2.4. Conclusions

In this paper the finite temperature behavior of the $(CO_2)_n$, $n = 6, 8, 13$, and 19, clusters has been investigated by means of parallel-tempering Monte Carlo simulations. The results have been analyzed in terms of inherent structure distributions and disconnectivity graphs. The question of when to characterize a structural transformation in a small cluster as a melting transition has been the subject of much discussion in the

literature.[24, 26-27] For the present purposes, in labeling a transition as "melting", we require that the transition display a pronounced, sharp peak in the heat capacity curve and that, over the range of temperatures corresponding to the rapid variation in the heat capacity, the system evolves from having appreciably population in a small number of low-energy structures to a having the population spread over a large number of higher-lying structures. We have further required that there be a sizable energy gap between the structures important on the low-temperature side of the heat capacity peak and those important on the high temperature side. Based on these criteria it is concluded that the sharp peaks near $T = 90$ K in the heat capacity curves of $(CO_2)_{13}$ and $(CO_2)_{19}$ are due to melting-type transitions whereas the broad peak in heat capacity curve of $(CO_2)_6$ should not be taken as indicative of melting. Although the broad peak in the heat capacity curve of $(CO_2)_8$ is similar in appearance to that of $(CO_2)_6$, these two clusters differ appreciably in the topologies of their potential energy surface as reflected in their disconnectivity graphs. However, due to the absence of a sizable energy gap between a group of low-energy structures and the higher-energy structures populated near $T = 70$ K, we conclude that $(CO_2)_8$ also does not undergo a well-defined melting transition. The broad shoulder near T = 50 K in the heat capacity curve of $(CO_2)_{19}$ is attributed to a "solid-solid-like" transition.
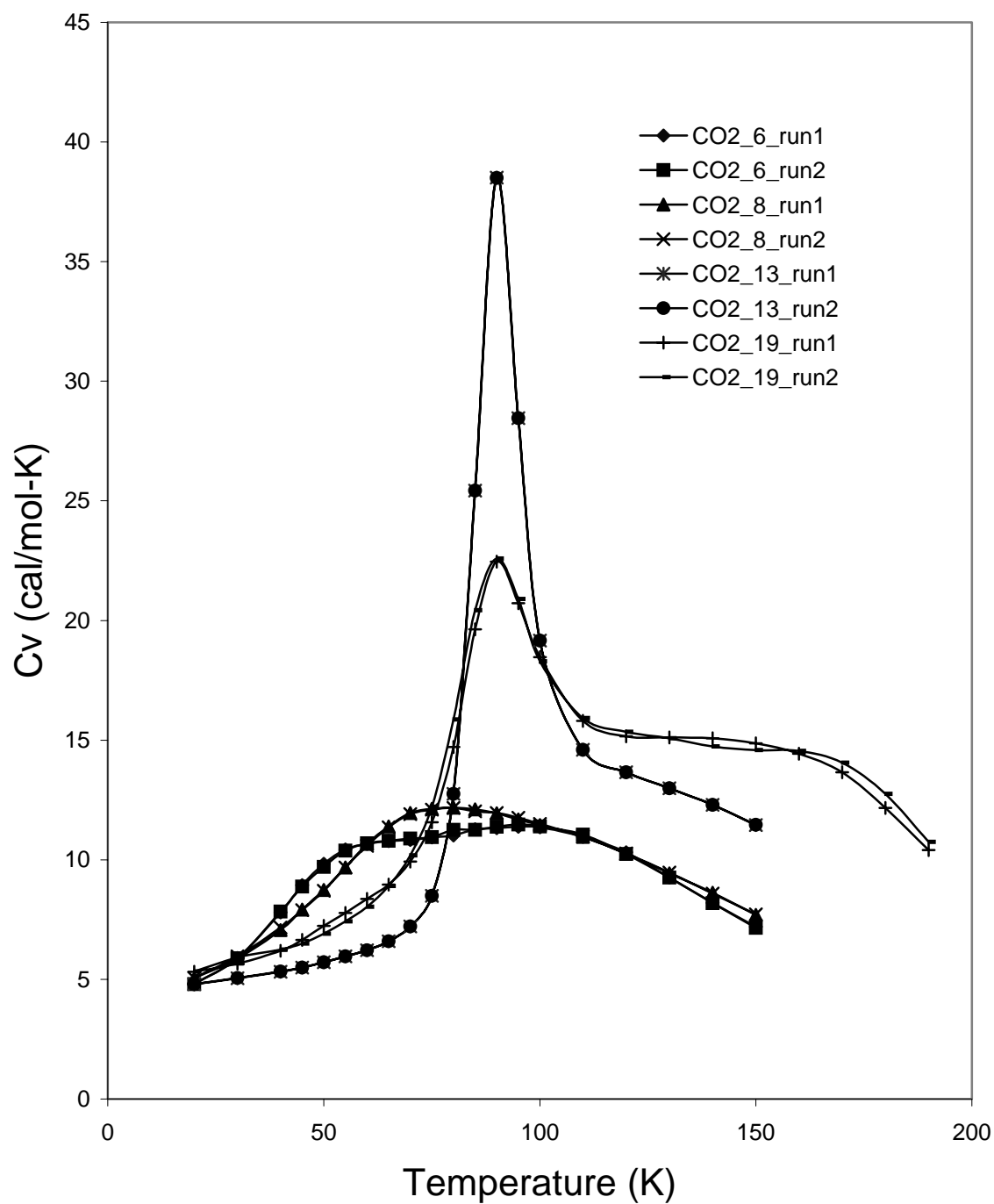
Figure 2.1 Heat capacity curves of the $(CO_2)_n$ clusters calculated by means of parallel tempering Monte Carlo simulations. For each cluster, run1 denotes the simulation starting from global minimum and run2 denotes the simulation starting from a random geometry.
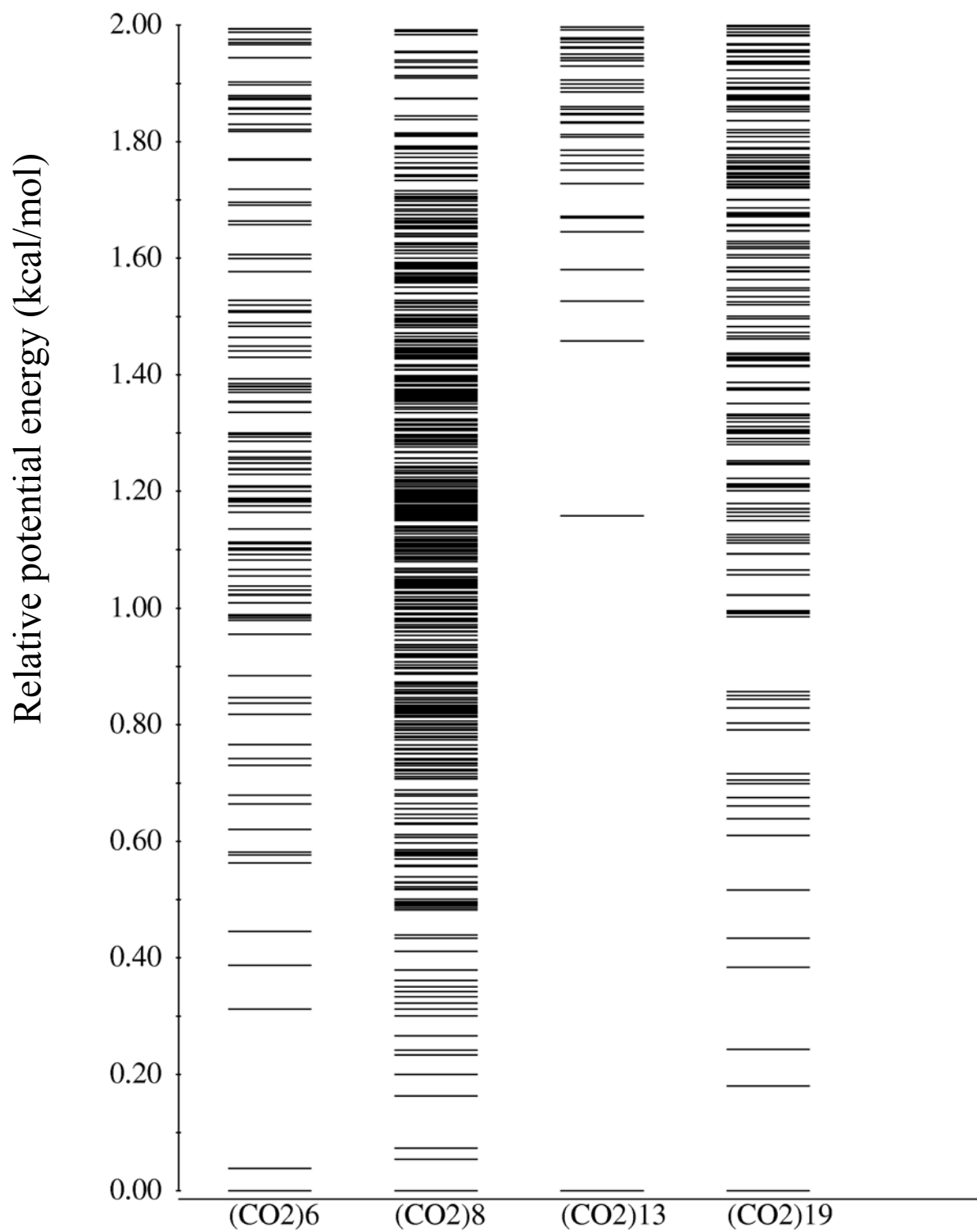
Figure 2.2 Energy level diagram for the $(CO_2)_n$ clusters. Each horizontal line corresponds to the energy of a local minimum as determined from quenching calculations.
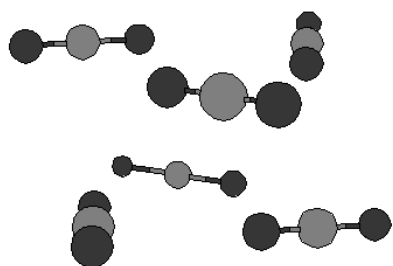
(1) -13.34 kcal/mol
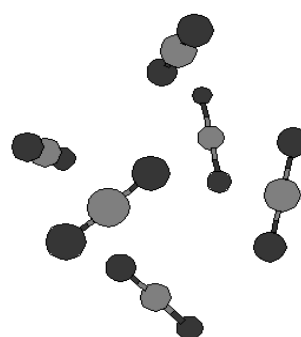
(2) -13.30 kcal/mol
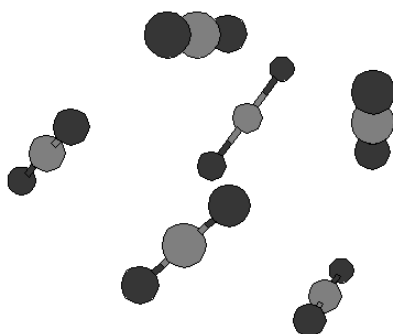
(3) -13.02 kcal/mol
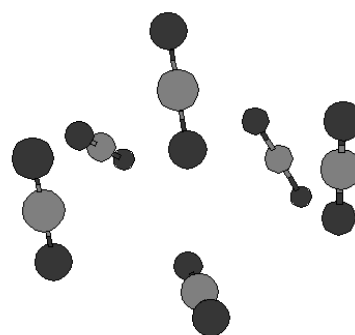
(4) -12.95 kcal/mol
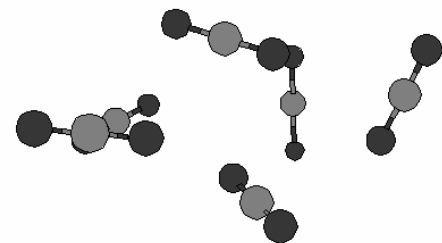
(5) -12.89 kcal/mol
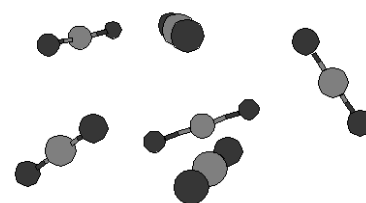
(6) -12.77 kcal/mol

Figure 2.3 Structures of the six lowest-energy minima of $(CO_2)_6$ from eigenmode-following optimizations.
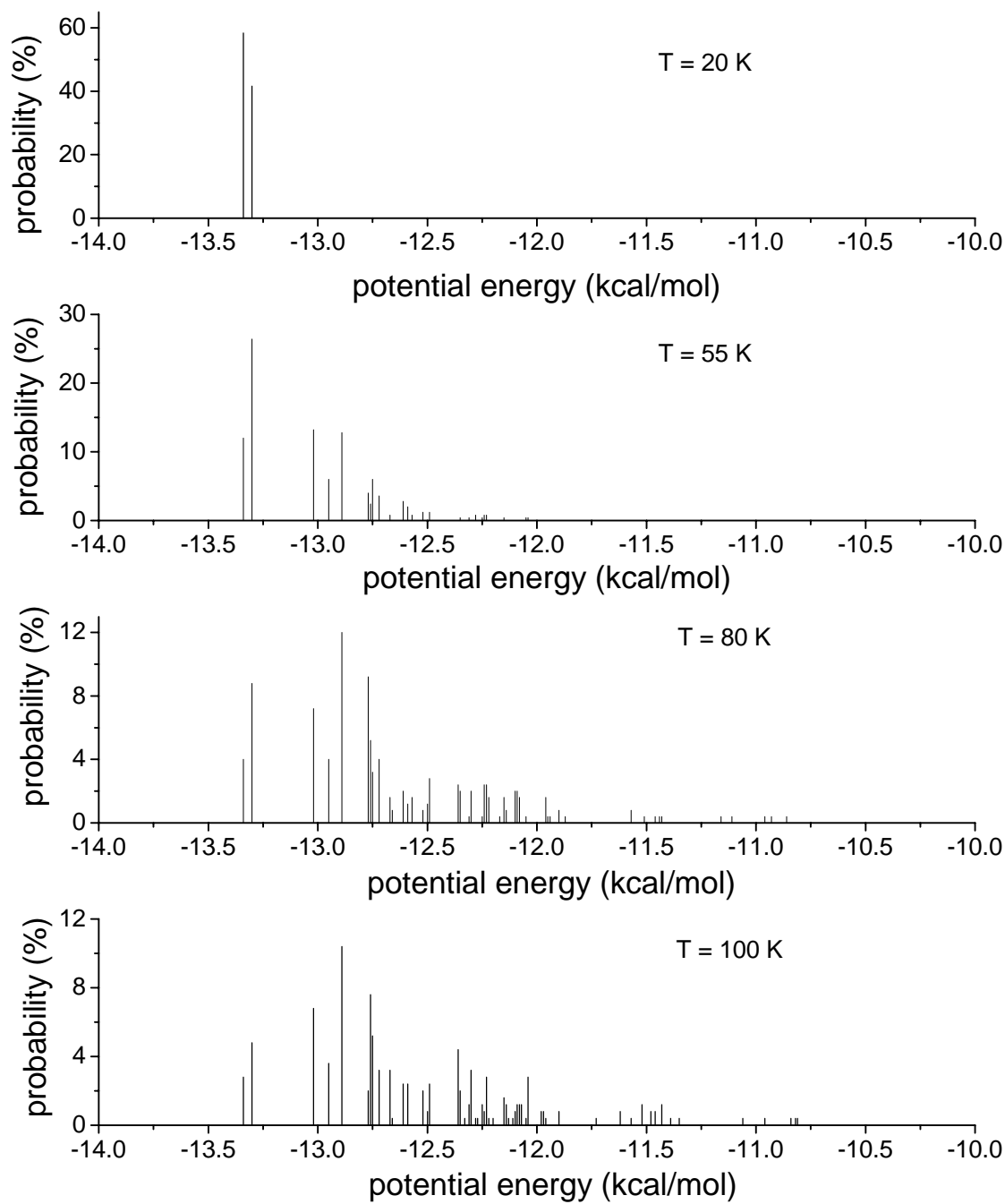
Figure 2.4 Distributions of local minima generated by quenching configurations from parallel tempering Monte Carlo simulations on $(CO_2)_6$.
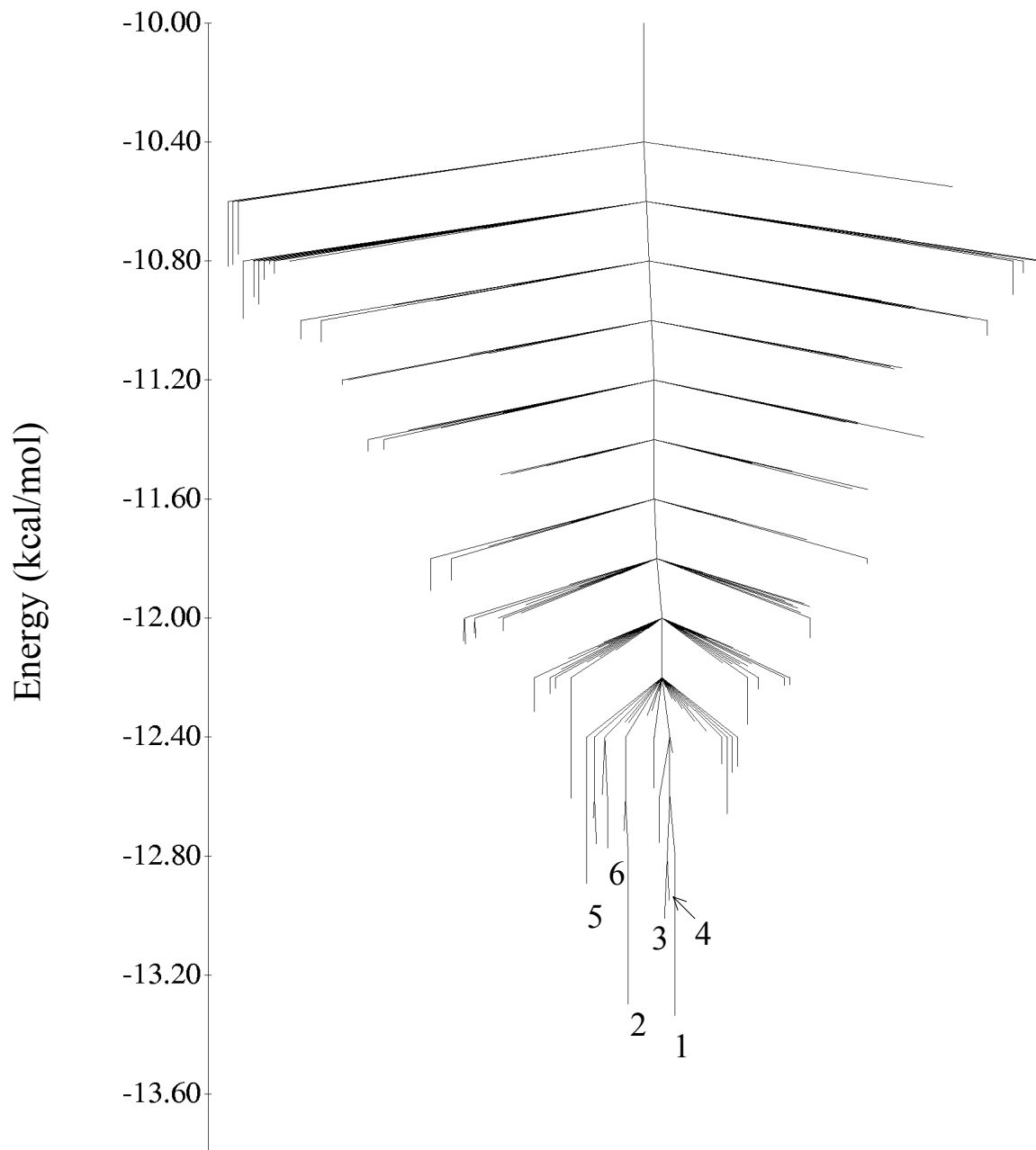
Figure 2.5 Disconnectivity graph for the $(CO_2)_6$ cluster. The numbers designate the low-energy structures depicted in Figure 2.3.
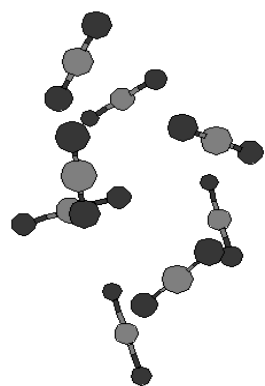
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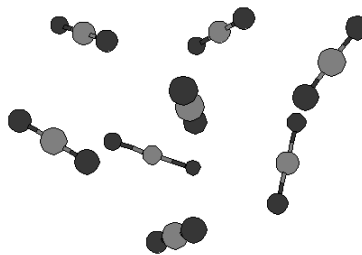
(2) -20.23 kcal/mol
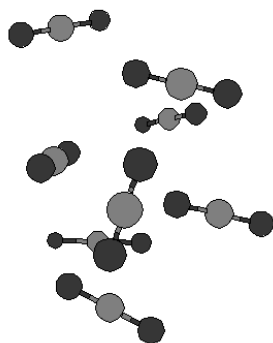
(3) -20.21 kcal/mol
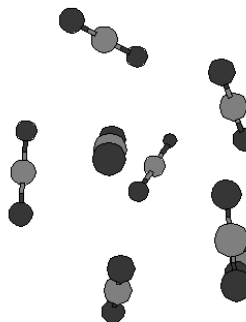
(4) -20.12 kcal/mol
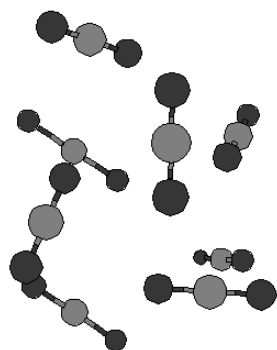
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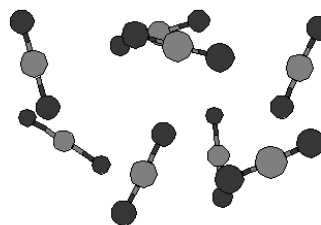
(6) -20.05 kcal/mol

Figure 2.6 Structures of the six lowest-energy minima of $(CO_2)_8$ from eigenmode-following optimizations.
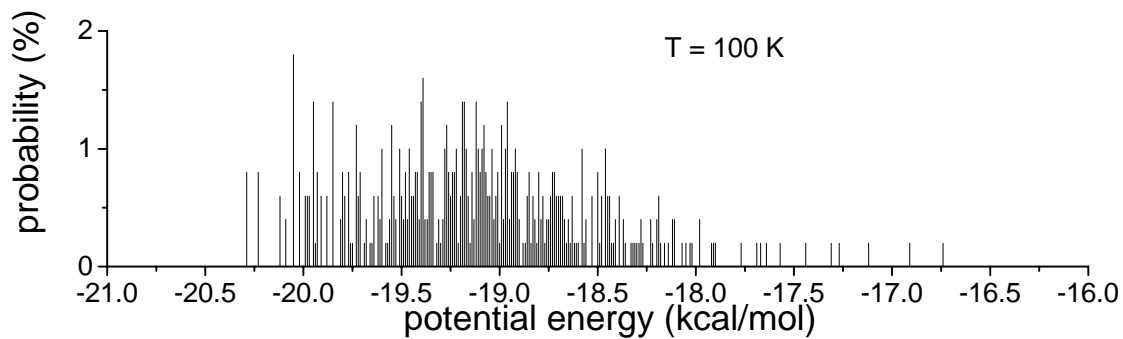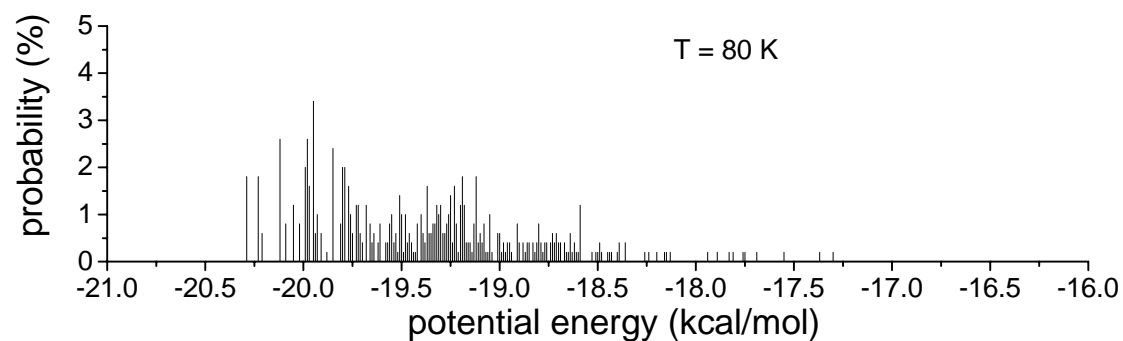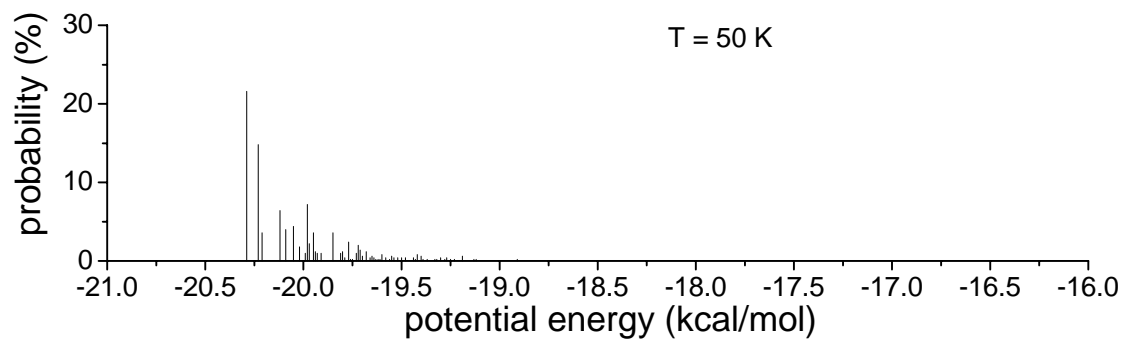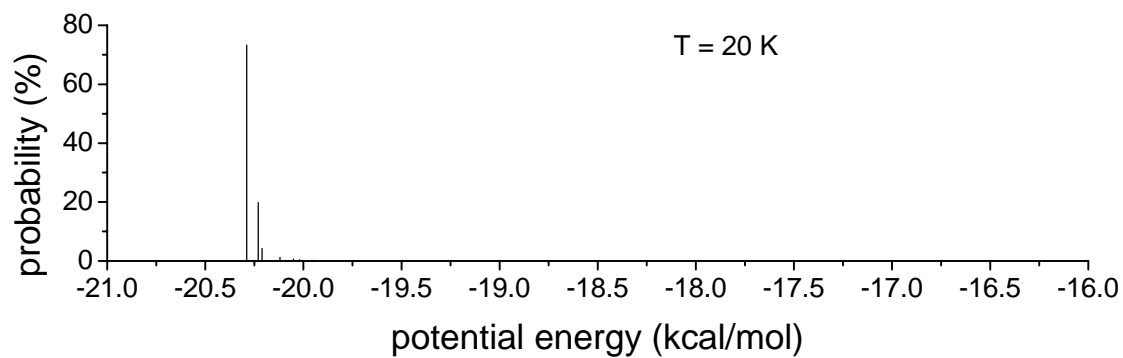
Figure 2.7 Distributions of local minima generated by quenching configurations from parallel tempering Monte Carlo simulations on $(CO_2)_8$.
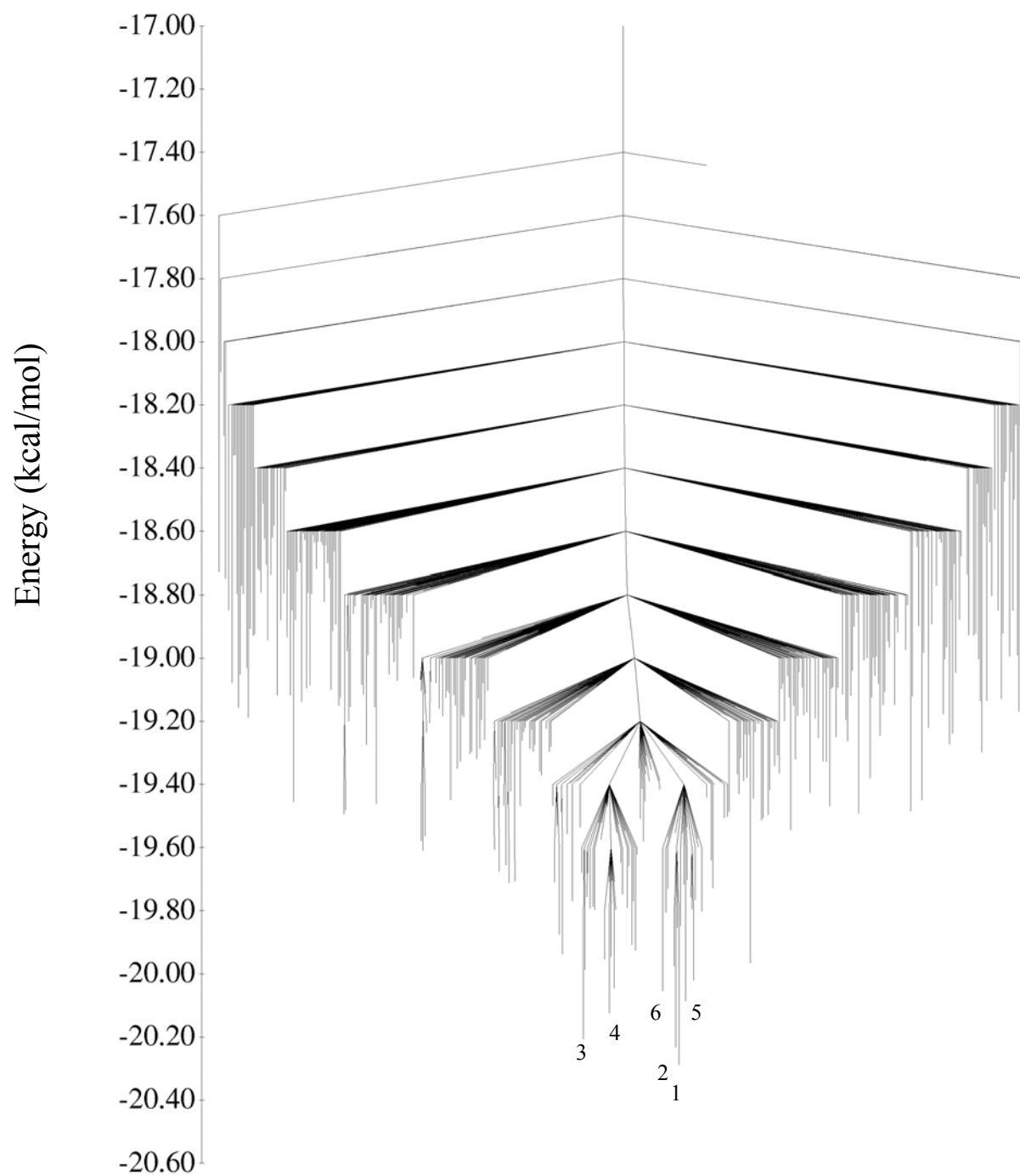
Figure 2.8 Disconnectivity graph for the $(CO_2)_8$ cluster. The numbers designate the low-energy structures depicted in Figure 2.6.
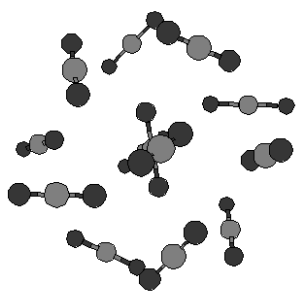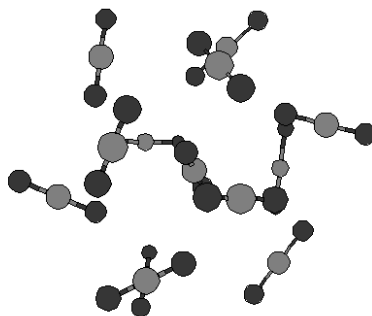
(1) -41.46 kcal/mol   (2) -40.30 kcal/mol
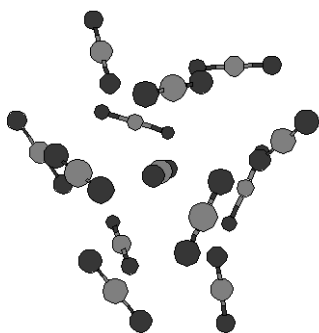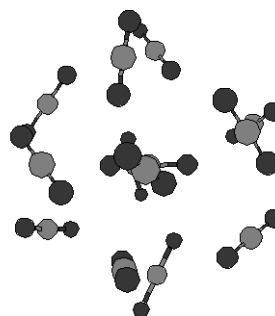
(3) -40.00 kcal/mol   (4) -39.93 kcal/mol
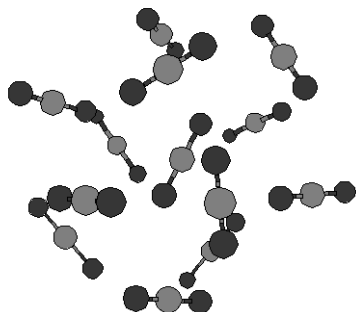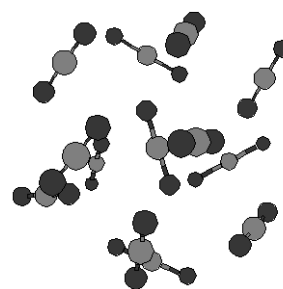
(5) -39.88 kcal/mol   (6) -39.81 kcal/mol

Figure 2.9 Structures of the six lowest-energy minima of $(CO_2)_{13}$ from eigenmode-following optimizations.
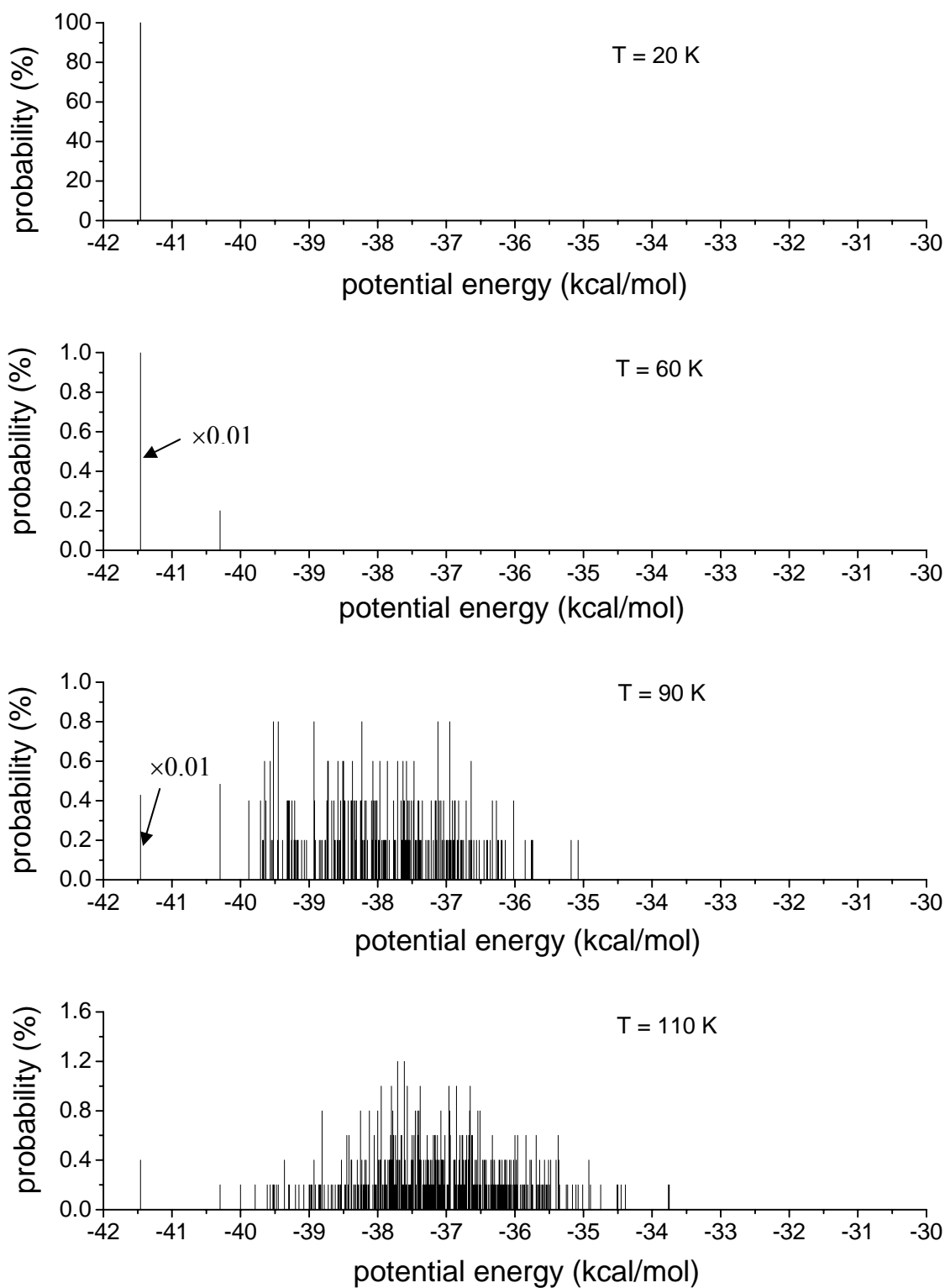
Figure 2.10 Distributions of local minima generated by quenching configurations from parallel tempering Monte Carlo simulations on $(CO_2)_{13}$.
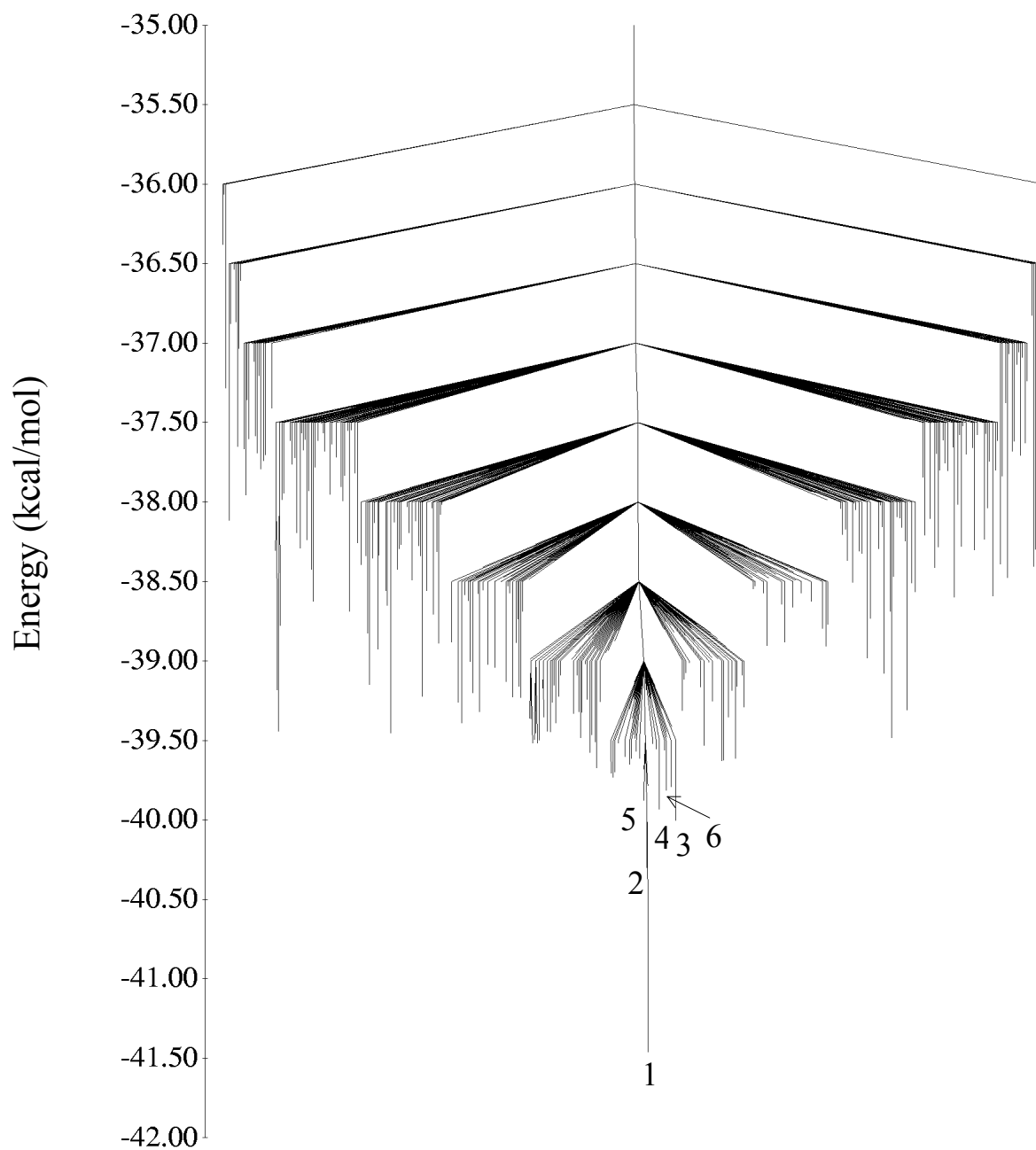
Figure 2.11 Disconnectivity graph for the $(CO_2)_{13}$ cluster. The numbers designate the low-energy structures depicted in Figure 2.9.
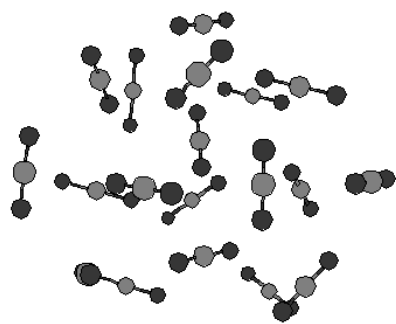
(1) -66.21 kcal/mol
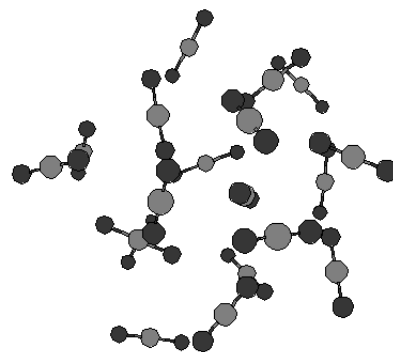
(2) -66.03 kcal/mol
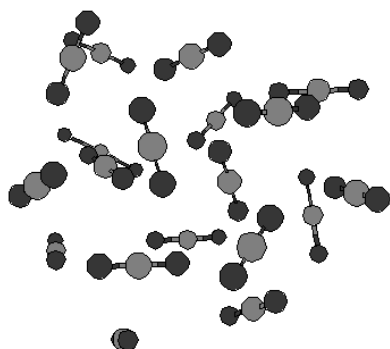
(3) -65.96 kcal/mol
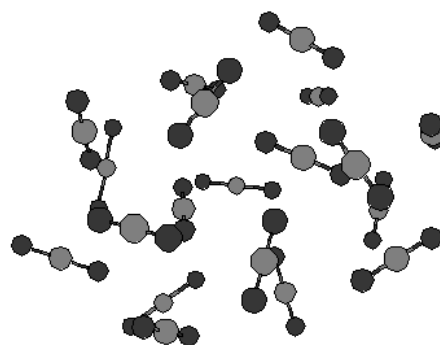
(4) -65.82 kcal/mol
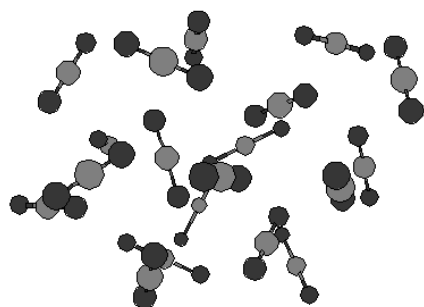
(5) -65.77 kcal/mol
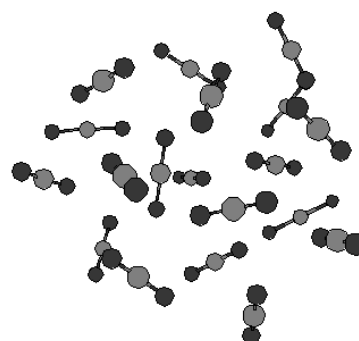
(6) -65.69 kcal/mol

Figure 2.12 Structures of the six lowest-energy minima of $(CO_2)_{19}$ from eigenmode-following

optimizations.
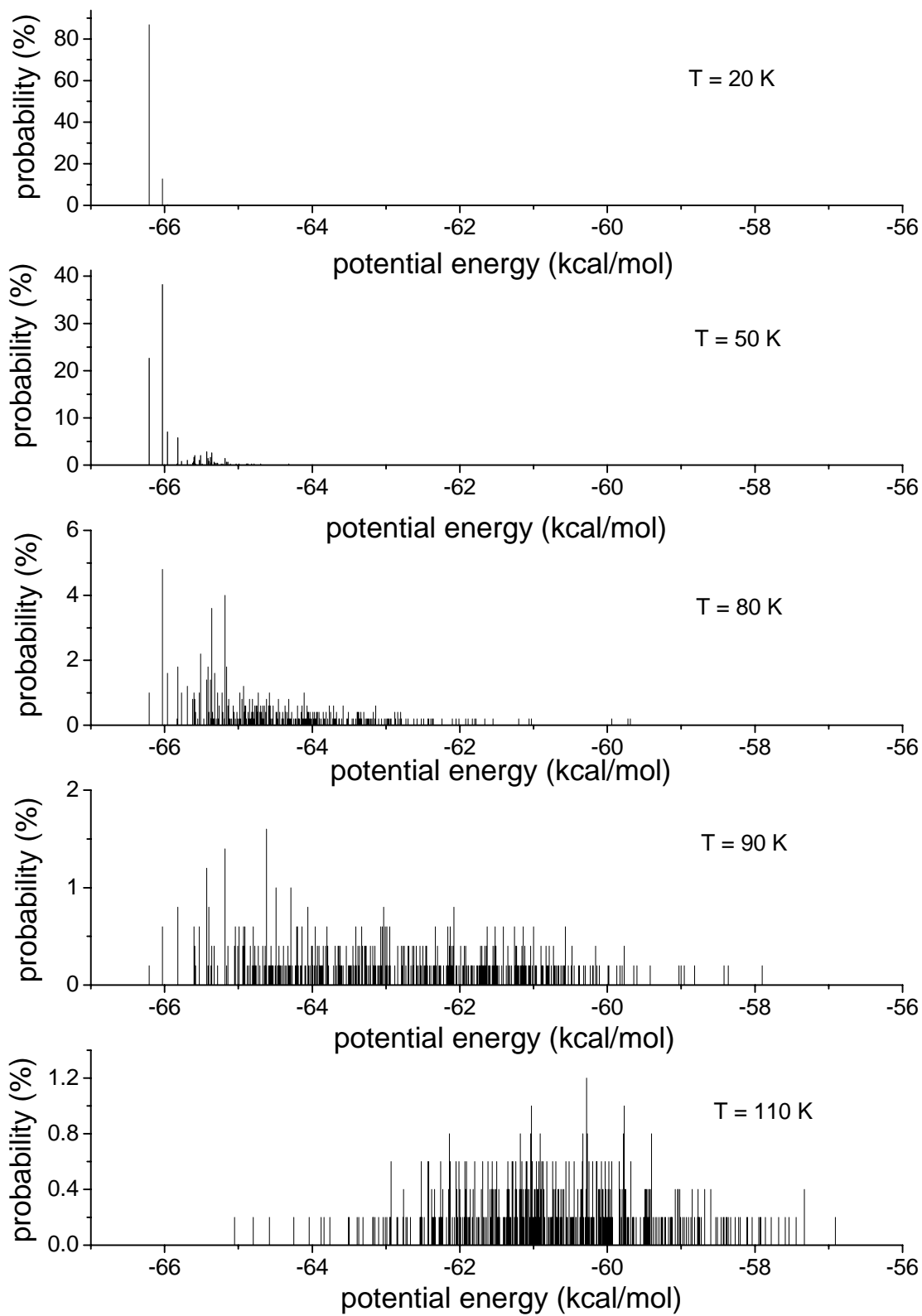
Figure 2.13 Distributions of local minima generated by quenching configurations from parallel tempering Monte Carlo simulations on $(CO_2)_{19}$.
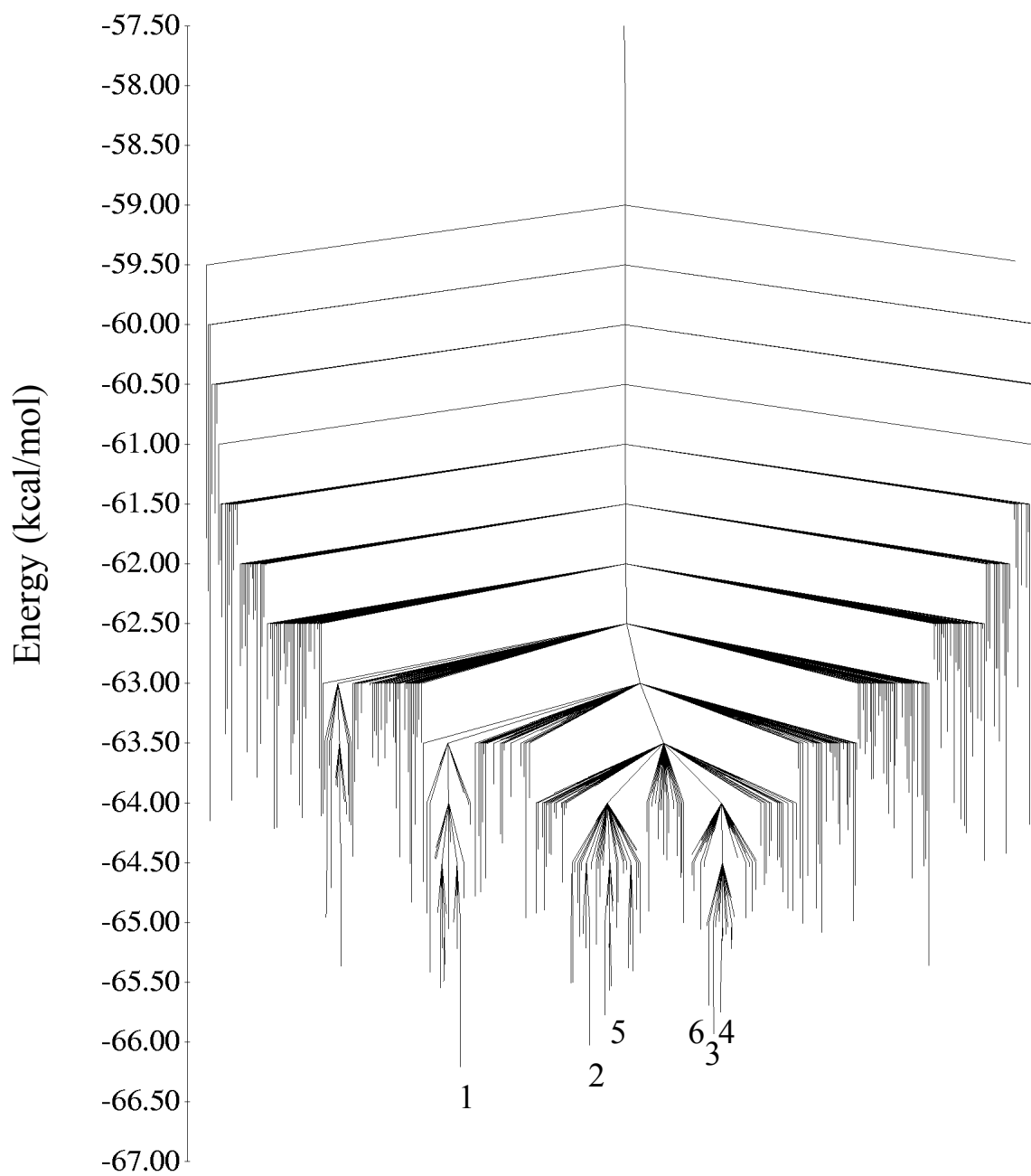
Figure 2.14 Disconnectivity graph for the $(CO_2)_{19}$ cluster. The numbers designate the low-energy structures depicted in Figure 2.12.
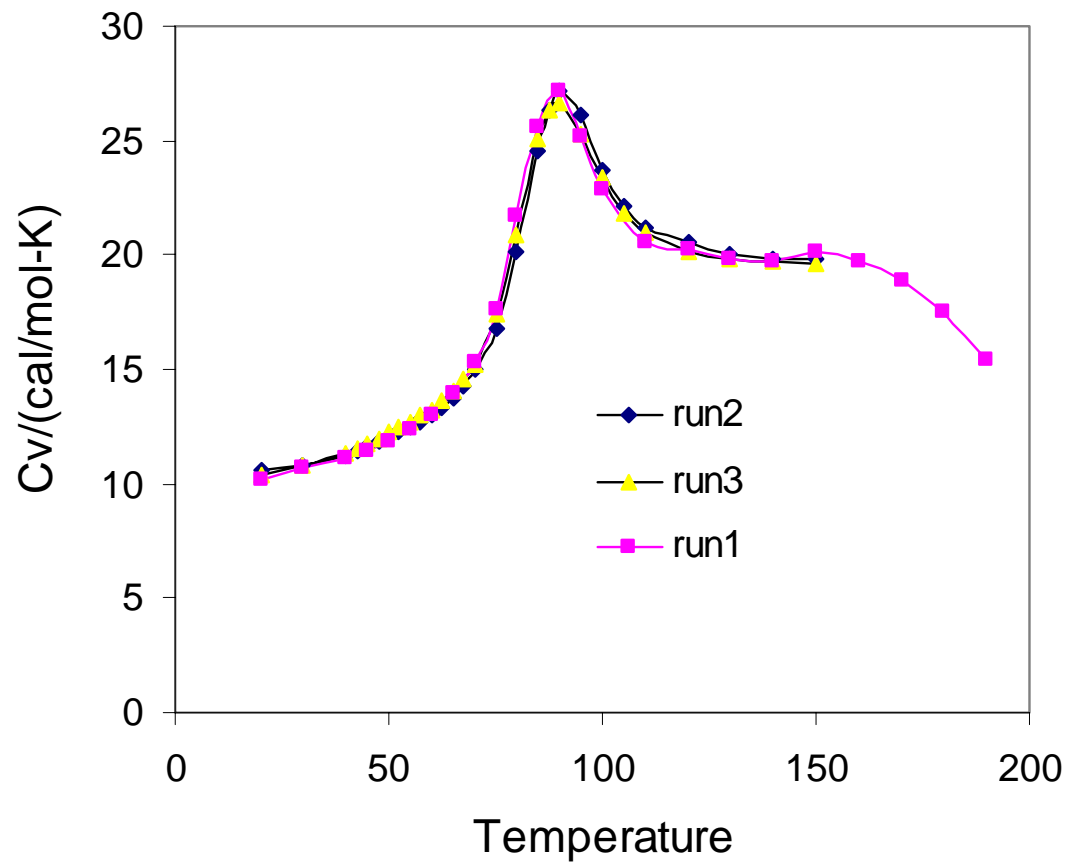
Figure 2.15 Heat capacity curves of $(CO_2)_{19}$ calculated by means of parallel tempering Monte Carlo simulations. The *run 1* denotes the simulations carried out with 24 temperatures spanning from 20 – 200 K, which is the same figure reported in Figure 2.1; *run 2* denotes the simulation carried out with 28 temperatures spanning from 20 – 150 K; *run 3* denotes the simulation carried out with the same temperature grid as *run 2*, but starting from a random geometry.
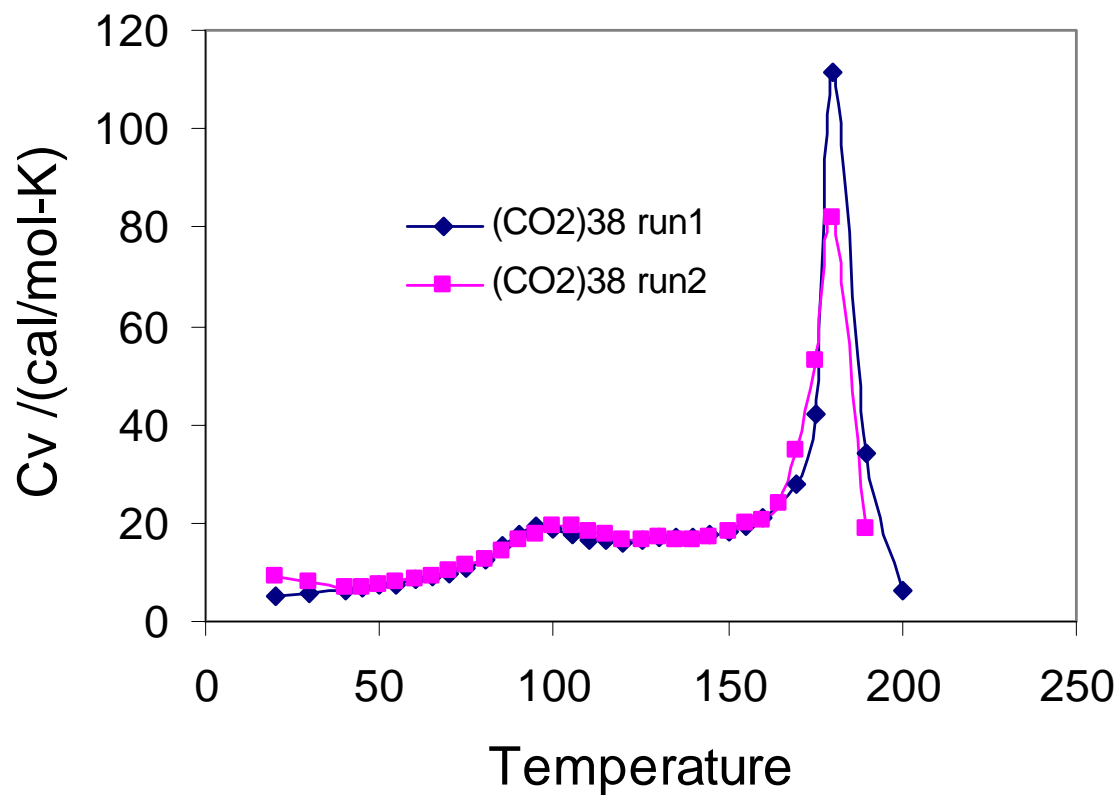
Figure 2.16 Heat capacity curves of $(CO_2)_{38}$ calculated by means of parallel tempering Monte Carlo simulation. Run1 and run2 denote simulations starting from different randomly picked starting geometries.

3.   Chapter 3 On the Convergence of Parallel Tempering Monte Carlo Simulations of LJ$_{38}$

3.1. Introduction

The conventional Metropolis algorithm for sampling the canonical distribution has difficulties dealing with the problem of quasi-ergodicity associated with complex potential energy landscapes. Recently, considerable progress has been made in developing efficient sampling algorithms for dealing with this problem. The parallel tempering algorithm has been used extensively as a means of improving sampling. However, it suffers from the need to use an increasing number of temperatures with increasing system size. The details of the parallel tempering algorithm were given in Chapters 1 and 2.

This chapter, describes an effective hybrid scheme for combining parallel tempering Monte Carlo and Tsallis generalized statistics. As mentioned in Chapter 1, Tsallis statistics employ more delocalized potential energy distributions than does sampling from the Boltzman distribution. Thus, the hybrid scheme might be expected to give improved convergence. The strategy is similar in spirit to work of Sugita *et al.*, who introduced a parallel tempering multicanonical algorithm[89,90]. Whitfield *et al*[91]. and Jang *et al*[92]. have previously combined parallel tempering with Tsallis statistics. In both their approaches, each replica at a specified target temperature is run with different *q* values. Exchanges of configurations are allowed between simulations with different *q* values but at the same *T*. Our hybrid scheme is an extension of the original parallel tempering Monte Carlo, with sampling being done in the Tsallis generalized ensemble at different temperatures, and the exchange of configurations between different replicas

(temperatures) being permitted. Results for the canonical ensemble are obtained by using the histogram reweighting to transform between ensembles.

Four different approaches – parallel tempering Tsallis statistics, parallel tempering Monte Carlo, Metropolis Monte Carlo, and Tsallis statistics based Monte Carlo - are applied to a 1D model potential and to the LJ_{38} cluster.

The 38-atom Lennard Jones (LJ_{38}) cluster has a global minimum with an O_h symmetry FCC-like structure followed by a C_{5v} symmetry icosahedral isomer lying only slightly higher in energy, see figure 3.2. These two minima are separated by a complicated rearrangement pathway with a high overall barrier. The funnel leading to the C_{5v} potential energy minimum is much broader than that leading to the FCC minimum,[85] and, as a result, it is difficult to locate the global minimum starting from an arbitrary structure and to achieve equilibrium in low temperature Monte Carlo simulations. For these reasons the LJ_{38} cluster has proven to be a valuable system for testing global optimization and Monte Carlo simulation algorithms.[71,93-95] Figure 3.1 shows the disconnectivity diagram of LJ_{38}.[74] This diagram helps convery a sense of the complexity of the potential energy surface of LJ_{38}.

The LJ_{38} cluster, with parameters appropriate for Ar, and referred to here as Ar_{38}, has been employed by Neirotti et al.,[71] Calvo et al.,[94] and Frantz[29] to demonstrate the utility of parallel-tempering Monte Carlo (PTMC) procedure[34,96-98] for achieving equilibrium in systems prone to quasiergodic behavior. The heat capacity curve of Ar_{38} as treated classically has a pronounced peak near T = 20 K due to cluster melting and a weak shoulder near T = 15 K due to the FCC → icosahedral transition. Traditional Monte Carlo simulations with Metropolis sampling[6] are unable to properly characterize the Ar_{38}

cluster at temperatures in the vicinity of the latter transition. Neirotti *et al.* were able to overcome this problem by use the PTMC procedure in which Monte Carlo simulations are carried out for a range of temperatures and exchanges of configurations between different temperature simulations (replicas) are permitted. The PTMC simulations of Neirotti *et al.* employed 32 temperatures (from 0.5 to 30 K), an equilibration period of 2.85×10^8 moves, and production cycles of 1.3×10^{10} moves at each temperature. Most moves for each replica were carried out using the Metropolis algorithm. An exchange of configurations between replicas at adjacent temperatures was attempted every 380 moves. PTMC simulations starting from the global minimum and from a randomly generated structure were found to give similar heat capacity (C_v) *vs.* *T* curves.

In testing a generalized ensemble PTMC algorithm, described below, we found that equilibration of Ar_{38} is much harder to achieve when starting the simulation from the C_{5v} minimum than from the global minimum. This led us to reexamine the convergence of traditional PTMC simulations of Ar_{38} starting from both the FCC global minimum and the C_{5v} local minimum. In addition, we present results obtained using a parallel tempering Monte Carlo algorithm based on Tsallis statistics[12-14] (PTTS).

3.2. Methodology

3.2.1. PTTS algorithm

In the Tsallis generalized ensemble[25-28] the entropy is defined as

$$S_q = k_B \frac{\int dr^N [1 - p_{Tsallis}(r^N)^{q-1}] p_{Tsallis}(r^N)}{q - 1}, \tag{3.2}$$

with the constraints

$$\int dr^N p_{Tsallis}(r^N) = 1, \text{ and } \int dr^N [p_{Tsallis}(r^N)]^q E(r^N) = \text{constant}, \tag{3.3}$$

where q is a parameter greater than 1.

The generalized probability is defined as

$$p_{Tsallis}(r^N) = \frac{1}{Z_q}[1-(1-q)\beta E(r^N)]^{1/(1-q)},$$ (3.4)

where

$$Z_q = \int dr^N[(1-(1-q)\beta E(r^N)]^{1/(1-q)}.$$ (3.5)

When $q \to 1$, the Tsallis distribution becomes the Boltzmann distribution.

The PTTS procedure carries out parallel tempering simulations with Tsallis weight functions. The implementation of the algorithm is similar to that of PTMC. The configurations are sampled with the distribution $[p_{Tsallis}(r^N)]^q$ using the effective energy

$$E_{eff} = \frac{q}{\beta(q-1)}\ln[1-(1-q)\beta(E-E_0)],$$ (3.6)

where E_0 is chosen so as to lie below the energy of the global minimum.

The probability of acceptance of moves within individual replicas in the PTTS algorithm is given by the usual Metropolis criterion

$$P_{i \to j} = \min(1, e^{-\beta(E_{eff\,j} - E_{eff\,i})}),$$ (3.7)

and that for exchanges of configurations between replicas m and n, is given by

$$P_{i \to j} = \min(1, e^{-\Delta}),$$

where (3.8)

$$\Delta = \beta_m(E_{eff\,j}^m - E_{eff\,i}^m) - \beta_n(E_{eff\,j}^n - E_{eff\,i}^n).$$

3.2.2. Reweight technology

Since the PTTS and TS simulations are carried out in a generalized ensemble, it is essential to transform back to the canonical ensemble in order to obtain physically meaningful values for the potential energy, heat capacity, and other properties of interest. This is accomplished by histogram reweighting. In the histogram method, the frequency of observing a energy range between bin is recorded which denoted H(E). E is the media value f the energy range in the bin. The probability of observing a particular value E is given by

$$P(E) = \frac{1}{Z} W(E) e^{-\beta E},$$
(3.9)

where β=1/(kT), Z is the partition function, and W(E) is the number of states with energy E.

If we generate N_c configurations, the expectation value of the number of occurrences of E is given by

$$H(E) = N_c Z^{-1} W(E) e^{-\beta E}$$
(3.10)

so

$$W(E) = H(E) Z e^{\beta E}.$$
(3.11)

Still consider the energy, the sampling over generalized Tsallis statics ensemble can be reweight as:

$$U = \langle E \rangle = \frac{\sum_E E H(E) e^{-\beta(E - E_{eff})}}{\sum_E H(E) e^{-\beta(E - E_{eff})}},$$
(3.12)

where E_{eff} is the effective energy is the Tsallis statistics.

The histogram procedure is very simple to implement, however the sum over all energy levels can result in overflows. This problem can be solved by the strategy of Ref

5, in which the terms in equation 3.12 are calculated using logarithms. The basic idea is: if l_1 and l_2 are the logarithms of two numbers x_1 and x_2, and that $l_1 \geq l_2$, then the logarithm of the sum $x_1 + x_2$ is

$$\log(x_1 + x_2) = \log(e^{l_1} + e^{l_2}) = \log(e^{l_1}(1 + e^{l_2 - l_1})) = l_1 + \log(1 + e^{l_2 - l_1}). \tag{3.13}$$

3.3. Computational details

3.3.1.   1D model potential

We wish to compare the rates of convergence of parallel tempering Monte Carlo (PTMC), parallel tempering Tsallis statistics (PTTS), Metropolis Monte Carlo (MMC) and Tsallis statistics (TS). To accomplish this, we employ a 1D-model potential as a test. Since the exact distribution can be calculated analytically for the model potential, the ergodicity can be readily monitored throughout the simulation. The potential energy function used is

$$V(x) = -50.0e^{-100(x+8)^2} - 47.5e^{-3(x-2)^2} - 50.0e^{-3(x-3)^2} + \sum_{n=1}^{4} 10C_n \sin(2n\pi x/10),$$

$$(3.14)$$

where x belongs to (-10, 10) and C_1, C_2, C_3, C_4 are chosen to be -0.466516, -0.834376, -0.714529, and -0.0245586, respectively. A plot of the potential energy function is shown in Figure 3.3, from which it is seen that it has two low-lying minima of almost the same energy, one with a narrow funnel (global minimum) and one with a broad funnel.

The exact distribution is calculated explicitly from the formula:

$$\rho_{exact}(x) = \frac{e^{-\beta V(x)}}{\int dx e^{-\beta V(x)}}. \tag{3.15}$$

The numerical distribution corresponding to a simulation of length *steps* is denoted by $\rho_{num}(x; steps)$. The ergodicity during the simulations is calculated using

$$\chi^2(steps) = \frac{\sum_x [\rho_{num}(x; steps) - \rho_{exact}(x)]^2}{\sum_x [\rho_{exact}(x)]^2} .$$

(3.16)

The simulations were carried out at temperatures of 24.0, 6.0, 1.5, 0.375, and 0.09375. In the PTMC and PTTS simulations exchanges between adjacent temperatures were attempted every 500 moves. The highest temperature used, 24.0, is high enough to avoid trapping even in the Metropolis MC simulations (as seen from Fig. 3.3). All simulations were carried out for 10^8 moves at each temperature. The maxima step sizes of the various simulations (MMC, TS, PTMC and PTTS) were adjusted to maintain a 50% acceptance ratio during the simulations. The q values in the Tsallis statistic and parallel tempering Tsallis statistics have been set to 1.1.

3.3.2. PTMC simulations of Ar$_{38}$

The PTMC simulations of Ar$_{38}$ carried out in the present study used the same 32 temperatures employed by Neirotti *et al.* Every 38th move an exchange of configurations from replicas at adjacent temperatures (T_i and T_{i+1}) was attempted, with T_i also being selected at random. This gave an attempted exchange rate of once every 38 x 31 moves, approximately three times less frequent than that used in the study of Neirotti *et al.* The remaining moves involved attempted displacements of individual atoms, selected at random and with acceptance/rejection being based on the Metropolis procedure. In carrying out PTMC simulations on cluster systems it is essential to exclude evaporative events. This was accomplished in the present study by using a constraint sphere with a radius of 8.5 Å. The maximum step sizes for the production runs were determined from

preliminary PTMC simulations in which the maximum step sizes were adjusted so that about 50% of the moves were accepted in each replica.

To monitor convergence, the simulations were carried out for different length equilibration periods, followed by production runs comprised of 10^9 move blocks. The equilibration periods ranged from 0.4×10^9 to 6.4×10^9 moves. The heat capacity for each simulation was calculated using

$$C_v = \frac{1}{kT^2}(\langle E^2 \rangle - \langle E \rangle^2).$$ \hfill (3.17)

For each replica, every millionth configuration was saved for subsequent analysis.

3.3.3. PTTS simulations of Ar_{38}

In our application of the PTTS algorithm we used the same temperature grid as employed for the PTMC simulations. Evaporative events were again excluded by using a 8.5 Å constraint sphere. After completion of the simulation, the energies were reweighted by using the histogram method[99] to transform back to the canonical ensemble.

Hansmann *et al.*[100] recommended choosing $q = 1+1/N$, where N is the number of degrees of freedom, in the system of interest. In the case of Ar_{38} this would give $q = 1.009$. However, we were unable to achieve well converged results for our PTTS simulations of Ar_{38} with a q value this large, and we adopted instead $q = 1.001$.

3.4. Results

3.4.1. 1D model potential

Figure 3.4 and 3.5 plot the ergodicity curves for the simulations carried out on the 1D model potential at different temperatures. The simulations were started from a

random position between x = 0 and x = 10, which are around the broad energy funnel. The distributions during the simulation are calculated using the histogram method. A total of 10,000 bins are used along the *x* axis, giving a bin size of 0.002. For *T* = 24 all simulation methods rapidly achieve equilibrium. At *T* = 0.094, neither Metropolis Monte Carlo nor Tsallis statistics sampling is able to achieve equilibrium even after 10^8 steps. In particular, in this case the system remains localized in the broad funnel, and is unable to sample the deeper, narrow funnel. In contrast, both PTMC and PTTS sample the Boltzmann distribution with a relative error of less than 1% even for s as short as 5×10^5 moves. For simulations longer than about 1×10^7 moves, PTTS performs significantly better than PTMC.

3.4.2. PTMC simulations of Ar$_{38}$

Figures 3.6 and 3.7 report the heat capacity curves obtained from the PTMC simulations initiated from the O$_h$ and C$_{5v}$ minima, respectively. The various curves were obtained from simulations with production periods of 1×10^9 moves, and with equilibration periods ranging from 0.4×10^9 to 6.4×10^9 moves. The curves from the simulations starting from the global minimum (Fig. 3.1) are in fairly good agreement with one another, with the greatest sensitivity to the length of the equilibration period being for temperatures near 12 K, *i.e.,* in the vicinity of the O$_h$ $\rightarrow$ icosahedral transformation. The agreement in this case is even better if we consider only the simulations with equilibration periods of 3.4×10^9 or more moves. The remaining small spread in the heat capacity curves near *T* = 12 K reflects the need for use of longer production runs.

From a comparison of Fig. 3.6 and 3.7 it is seen that the agreement between the heat capacity curves from the various simulations started from the C_{5v} minimum is much poorer than that found between the heat capacity curves from the various simulations started from the O_h minimum. In particular, when starting from the C_{5v} minimum, the simulations employing equilibration periods of 0.4×10^9, 1.4×10^9, and 2.4×10^9 moves display a spurious peak at temperatures below that anticipated for the $O_h \rightarrow$ icosahedral transformation. This peak is especially pronounced in the simulation with an equilibration period of only 0.4×10^9 moves, where it appears near 3 K. The spurious peak moves up in temperature and decreases in height as the equilibration period is increased, approaching the physically meaningful shoulder near $T = 12$ K for equilibration periods of 3.4×10^9 or more moves. However, even when using these longer equilibration periods, the heat capacity curves from the various simulations show more scatter, especially in the region of the $O_h \rightarrow$ icosahedral transformation, when starting from the C_{5v} than from the O_h minimum. This indicates that the need for a longer production period is more acute when starting the simulation from the C_{5v} minimum.

Figure 3.8 displays heat capacity curves obtained from PTMC simulations starting from the global minimum and from the C_{5v} minimum, with equilibration periods of 3.4×10^9 moves and averaging over four consecutive blocks of 1×10^9 production moves. The two heat capacity curves are in close agreement with one another as well as with that published previously by Neirotti *et al.* even in the region of the shoulder due to the $O_h \rightarrow$ icosahedral transformation. However, the agreement is deceptive as is revealed by comparing with the results obtained from still longer simulations with averages calculated using the configurations sampled in the moves between 7.4×10^9 and 11.4×10^9

and between 11.4×10^9 and 17.4×10^9. For the case that the simulations were started from the global minimum, the resulting heat capacity curves are nearly identical to that obtained by averaging over the configurations sampled over the moves 3.4×10^9 to 7.4×10^9 and which is shown in Fig. 3.8. On the other hand, in the case that the simulations were started from the second lowest energy minimum, the heat capacity curve obtained by averaging over configurations sampled in the 7.4×10^9 to 11.4×10^9 range of moves is much more pronounced than that reported in Fig. 3.8, whereas that obtained by averaging over moves in the $11.4 \times 10^9 - 17.4 \times 10^9$ range is similar to that reported in Fig. 3.8. These results show that very long production runs are required to achieve convergence of PTMC simulations in the vicinity of the $O_h \rightarrow$ icosahedral transformation when starting from the C_{5v} minimum.

Additional insight into the origin of the difficulty in converging the PTMC simulations of LJ_{38} when starting from the C_{5v} minimum can be gained by determining the inherent structures associated with the configurations present at the end of each equilibration period. The inherent structures were obtained by optimized the structures with the eigenmode-following algorithm as implemented in the Orient program.[101] Figure 3.9a reports for the simulations starting from the global minimum the energies of the resulting inherent structure at the end of various equilibration periods. The resulting inherent structure distributions are similar for various length equilibration periods, with the first ten replicas (*i.e.,* those for the ten lowest temperatures) giving the global minimum and at most three of the 17 lowest temperature replicas giving an inherent structure other than the global minimum. Similar results are found for the inherent structures populated at the end of the production runs for the simulations starting from the

C_{5v} local minimum for the cases of equilibration periods of 3.4×10^9 or more moves. (Fig. 3.9b) However, in the simulations with equilibration periods of 2.4×10^9 or fewer moves, fewer low-temperature replicas have inherent structure associated with the global minimum at the end of the equilibration runs. In fact, with the equilibration period of only 0.4×10^9 moves, only the lowest temperature replica is associated with the global minimum inherent structure at the end of the equilibration. As the production runs increase from 4×10^8 to 3.4×10^9 moves, the number of low-temperature replicas associated with the global minimum at the end of the run increases. The spurious low-temperature peak in the heat capacity curve in the simulations starting from the second lowest energy minimum structure and with equilibration periods of less than 3.4×10^9 moves, is a consequence of the global minimum structure not being adequately sampled in the equilibration runs in the low-temperatures replicas. In these cases, during the course of the production runs, there is a shift in the population in the low temperature replicas from minima in the icosahedral funnel to the O_h funnel. This shift in population is responsible for the spurious low-temperature peak in C_v. While this problem could be overcome by use of very long production cycles, this is less computationally efficient than using equilibration runs of adequate length.

We next examine the distributions of inherent structures obtained from the production runs associated with PTMC simulations starting from both the global minimum structure as well as from the C_{5v} minimum. Fig. 3.10 shows the distributions obtained for the simulations started from the C_{5v} local minima, using production runs of 1×10^9 moves, and employing various length equilibration periods. For each simulation, every millionth configuration was saved and optimized to its inherent structure. It is clear

from the results reported in this figure that the simulations using equilibration periods of only 1.4×10^9 and 2.4×10^9 moves are far from converged.

Fig. 3.11 reports the distributions of inherent structures from simulation starting from the O_h and C_{5v} minima, and carried out for equilibration periods of 3.4×10^9 moves and production periods of 4×10^9 moves. The inherent structure distributions from these two simulations are nearly identical although, as pointed out above, simulations starting from the second lowest energy minimum are not actually converged. The population of low-energy structures associated with the icosahedral funnel grows rapidly as the temperature increases from about 10 K, and reaches a maximum around 18 K. Interestingly, both the third and fifth lowest energy isomers of Ar_{38} acquire considerably more population than does the second-lowest energy (C_{5v}) isomer. At T = 18.5 K, 65% of the total population is associated with the four-lowest energy inherent structures associated with the icosahedral funnel.

3.4.3.   PTTS simulations of Ar_{38}

Figure 3.12 shows the heat capacity curves obtained from the PTTS simulations of Ar_{38} initiated from the second lowest energy minimum. The equilibration periods ranged from 0.4 to 3.2×10^9 moves and the production cycles were either 1.0×10^9 or 0.6×10^9 moves. PTTS simulations with an equilibration period as short as 2.0×10^9 moves and a production period as short as 0.6×10^9 moves, give a nearly converged C_v vs. T curve, with the exception being that the shoulder near 12 K is slightly more pronounced than found from the PTMC simulations starting from the global minimum. Upon adoption of an equilibration period of 3.2×10^9 moves, while remaining a production period of only 0.6×10^9 moves, the low-temperature shoulder is attenuated, bringing it more in line with

the results from the PTMC simulations starting from the global minimum structure. The more rapid convergence of the PTTS simulations compared to the PTMC simulations may be a consequence of the broader potential energy distributions associated with the former.

3.5. Conclusions

The present study demonstrates that it is much more difficult to achieve equilibrium in PTMC simulations on the Ar_{38} cluster when starting from the second lowest energy minima than when starting from the global minimum. Although not discussed in the text, we have also found that simulations starting from the third lowest energy minimum, which like the second lowest energy isomer is associated with the icosahedral funnel, also require long production and equilibration periods to achieve convergence. We anticipate that this is also the case for other low-energy minima associated with the icosahedral funnel. It is known from the work of Wales and Doye[102] that starting from an arbitrary structure it is easier to locate the C_{5v} than the O_h minimum of LJ_{38}. Based on the results of the present study, we conclude that it is more difficult to escape from the C_{5v} minimum than from the O_h minimum. This is consistent with the finding of Wales,[103] who, using information on the minima and transition states of LJ_{38}, calculated rates for escaping from these two minima, and is a consequence of the O_h minimum being associated with a narrow funnel and the C_{5v} minimum with a broad funnel on the potential energy surface. Thus the LJ_{38} cluster with the initial configuration chosen to be a minimum in the icosahedral funnel should serve as a valuable test case for new Monte Carlo simulation algorithms.

A new algorithm combining parallel tempering Monte Carlo and Tsallis statistics is introduced and tested on a 1 – dimensional model potential and on LJ_{38}. The model potential results demonstrate significantly better convergence of the PTTS algorithm than for the PTMC algorithm. The PTTS algorithm also displays improved convergence in the case of LJ_{38}. Further work is needed to determine whether this hybrid algorithm will in fact require fewer temperatures than does the PTMC algorithm.
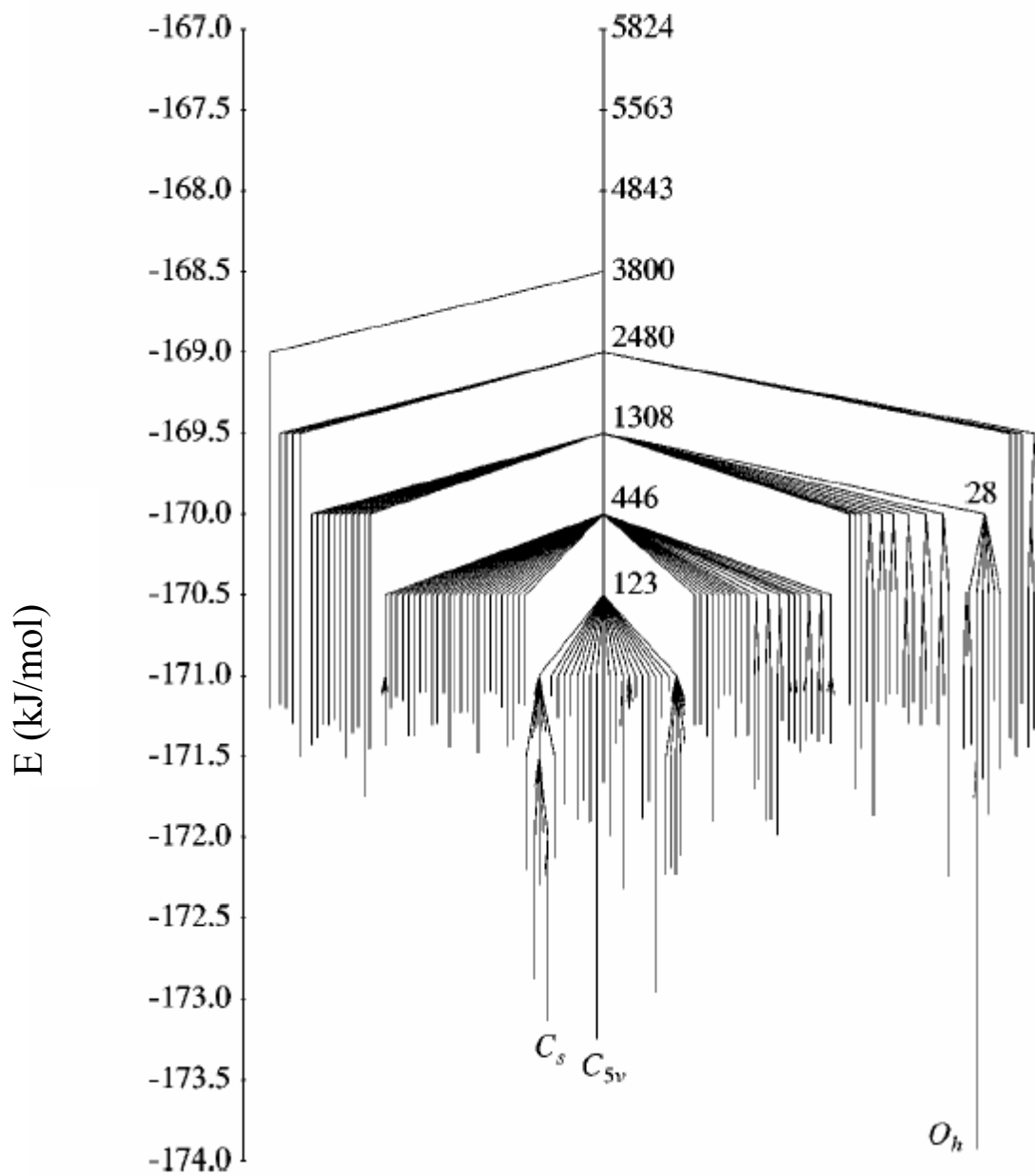
Figure 3.1 Disconnectivity diagram of Ar_{38}.
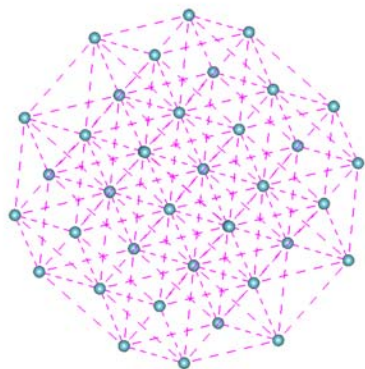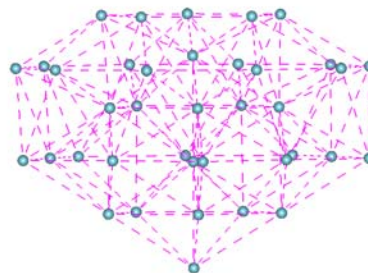
Oh structure   C5v structure

Figure 3.2 Two lowest energy isomers of Ar_{38}.
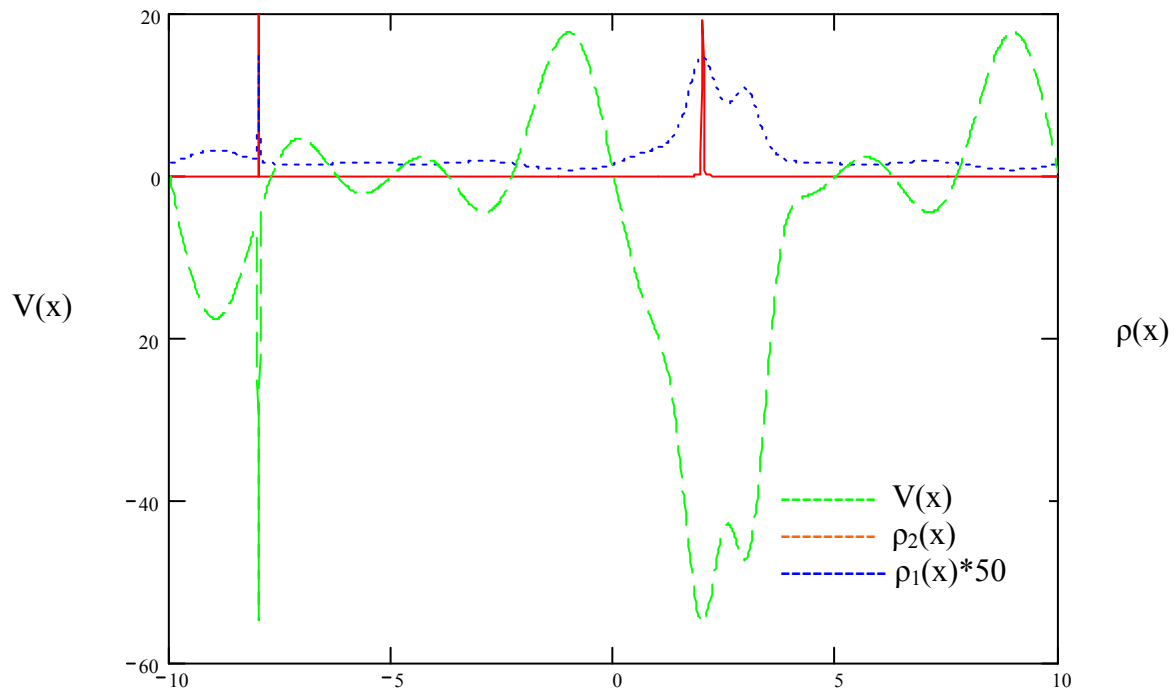
Figure 3.3 One-dimensional potential energy V(x) *vs.* position *x* and the analytical distributions ρ_1 and ρ_2 at $T = 24$ and 0.094, respectively.
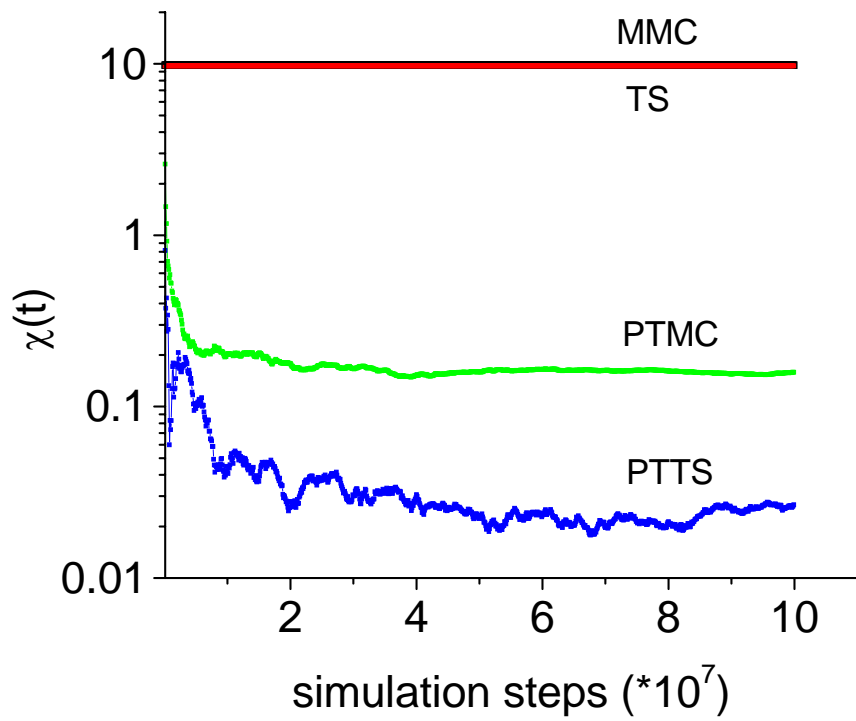
Figure 3.4 Ergodicity of the various simulation methods for the one-dimensional model and T= 0.093. MMC denotes Metropolis Monte Carlo algorithm, TS denotes Tsallis statistics, PTMC denotes parallel tempering Monte Carlo, and PTTS denotes parallel tempering Tsallis statistics.
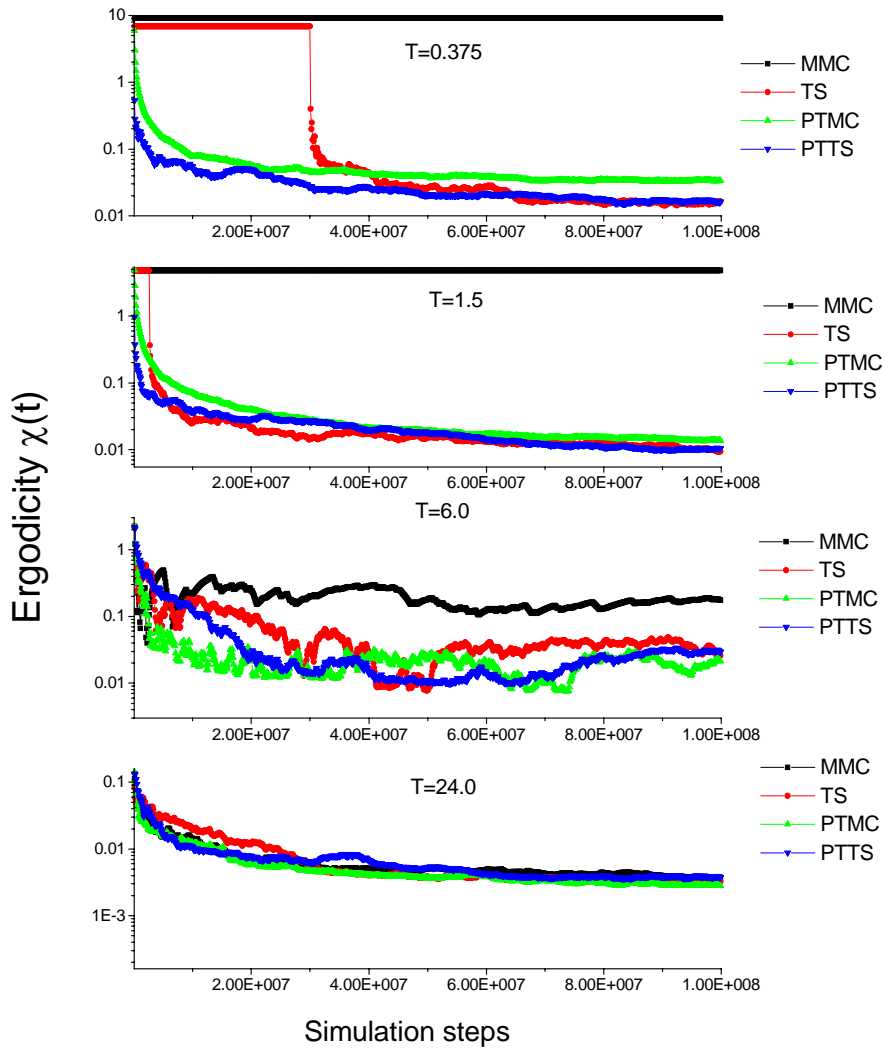
Figure 3.5 Ergodicity for the various simulation methods for the one-dimensional model at different temperatures. MMC denotes Metropolis Monte Carlo algorithm, TS denotes Tsallis statistics, PTMC denotes parallel tempering Monte Carlo, and PTTS denotes parallel tempering Tsallis statistics.
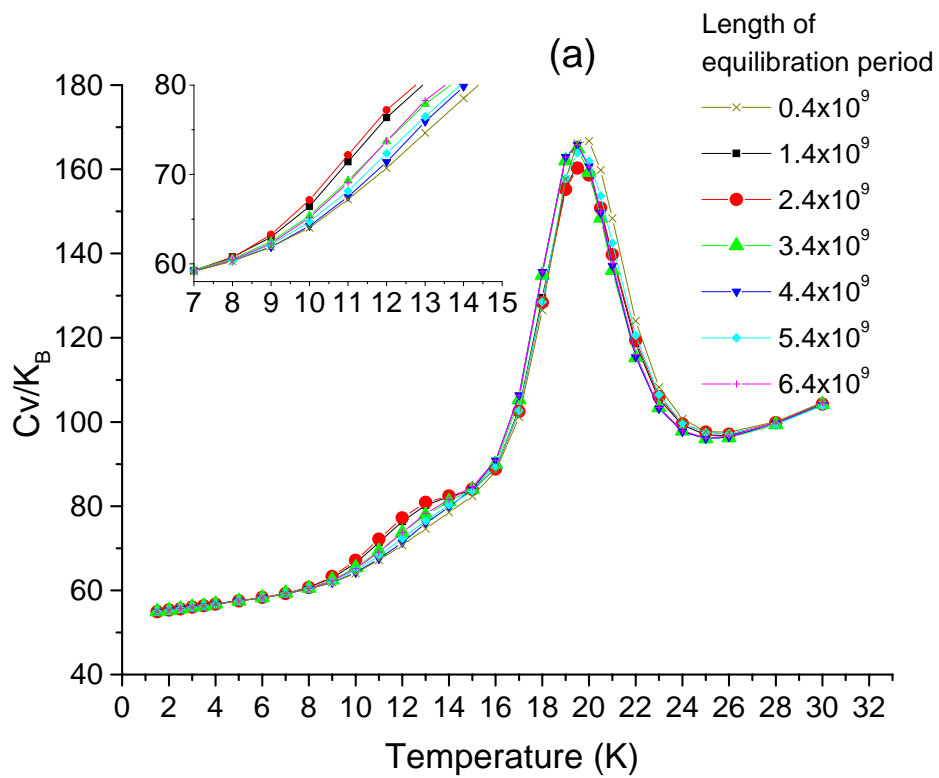
Figure 3.6 Heat capacity *vs. T* of Ar$_{38}$ from PTMC simulations starting from the global minimum isomer. All production runs were carried out for 1 billion moves. Equilibrium periods ranged from 0.4 to 6.4x10^9.
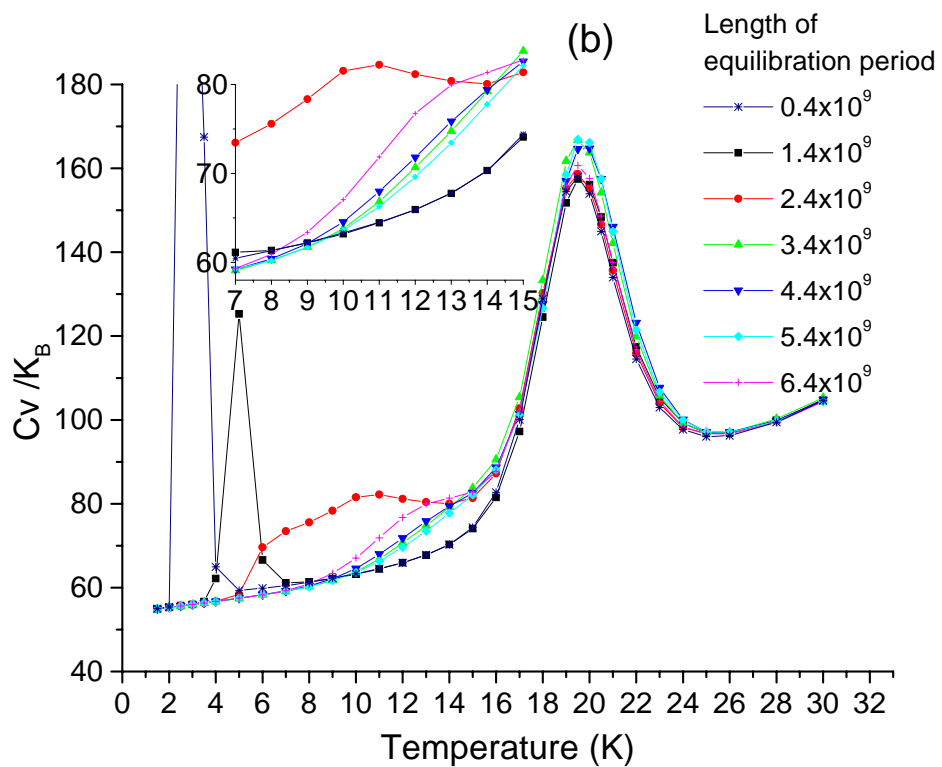
Figure 3.7 Heat capacity *vs.* *T* of Ar$_{38}$ from PTMC simulations starting from second lowest energy minimum isomer. All production runs were carried out for 1 billion moves. Equilibrium periods ranged from 0.4 to 6.4x10^9.
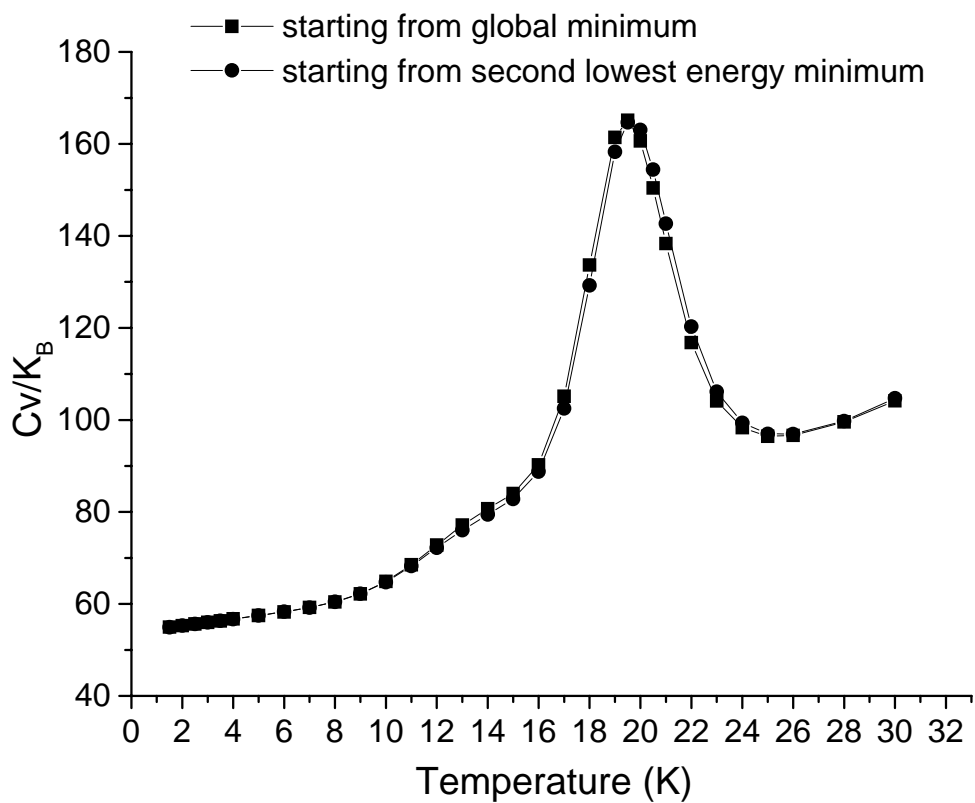
Figure 3.8 Heat capacity *vs. T* of Ar$_{38}$ from PTMC simulations starting from the global minimum and from the second lowest energy isomer. The equilibrium periods were 3.4×10^9 moves, and the production runs were carried out for 4×10^9 moves.
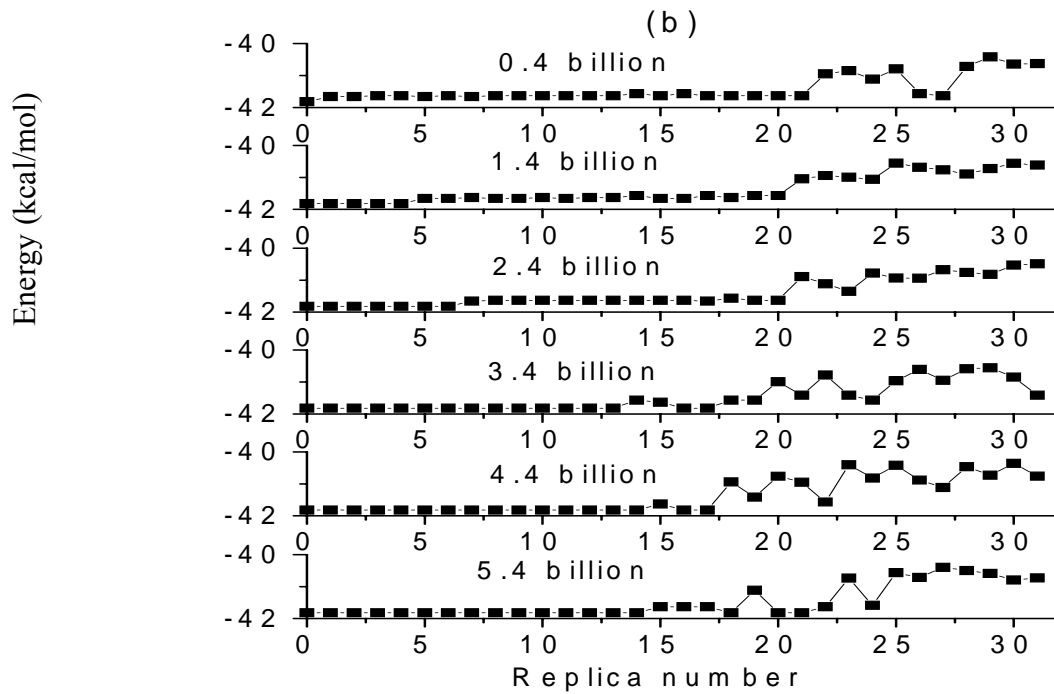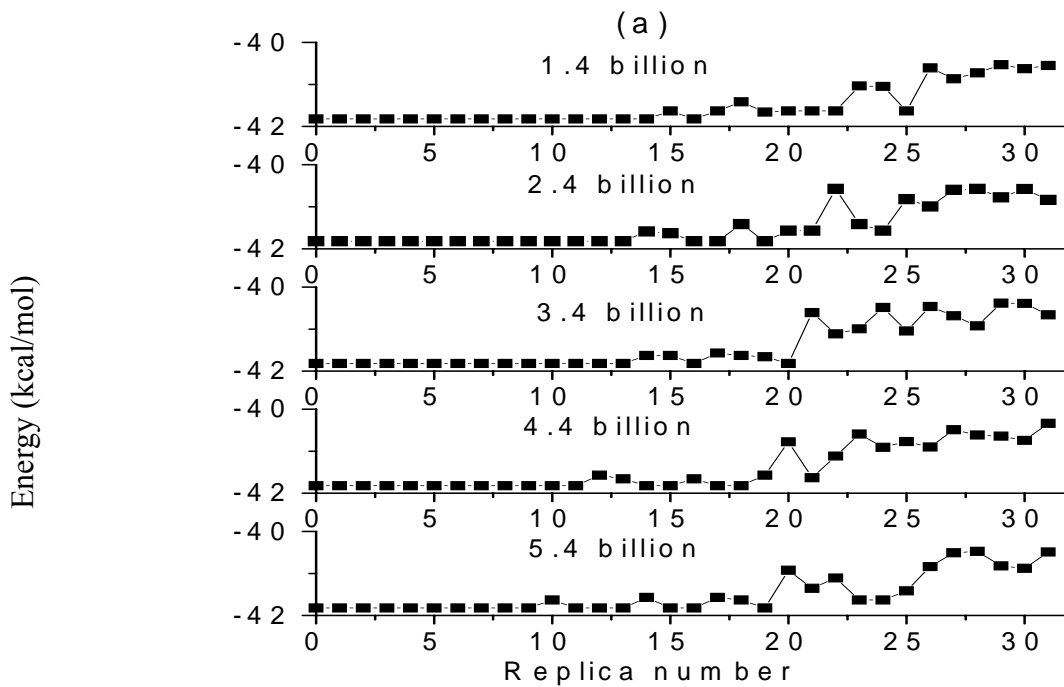
Figure 3.9 Inherent structures at the end of various length equilibration periods for PTMC simulations of Ar$_{38}$: (a) starting from the global minimum, (b) starting from the second lowest energy minimum. The number of moves in each equilibration period is specified in the figure.
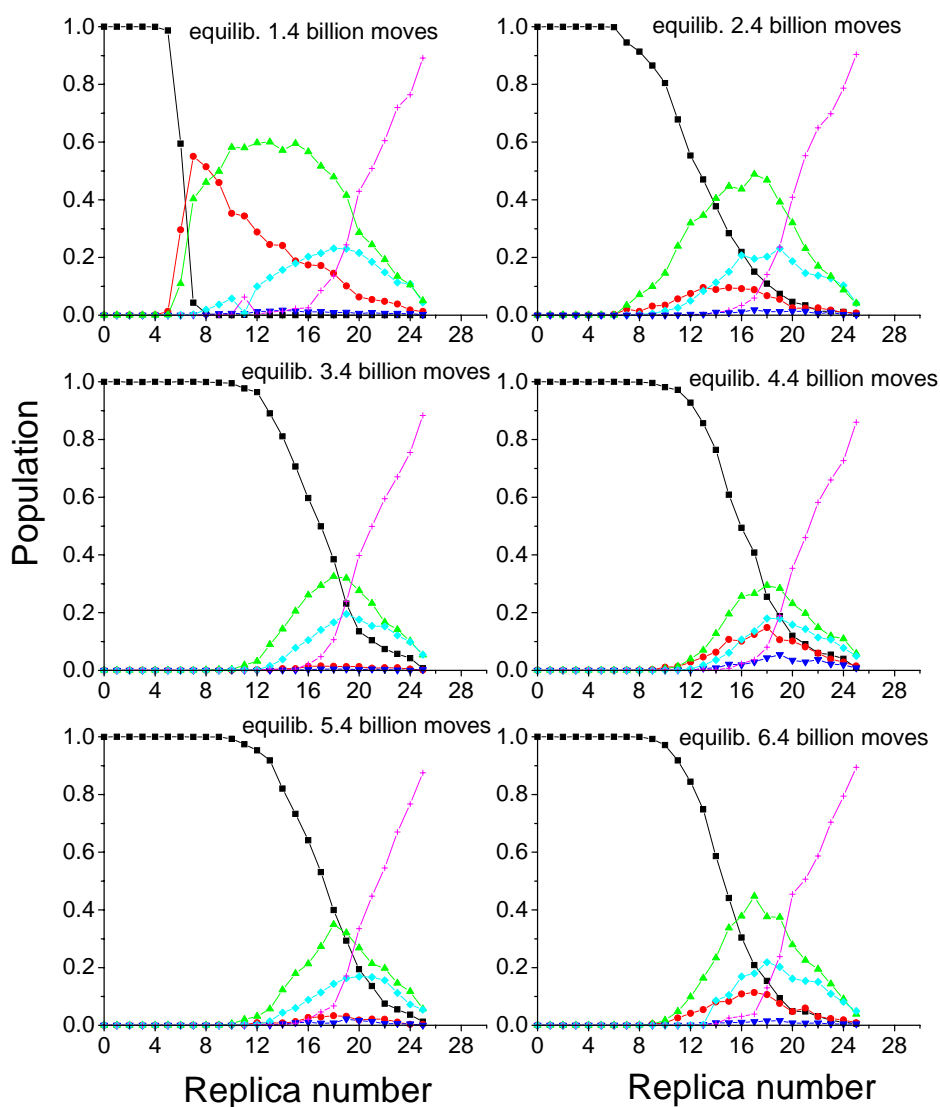
Figure 3.10 Inherent structure distributions from PTMC simulations of Ar_{38} starting from the second lowest energy minimum. Simulations were carried out with a production period of 1×10^9 moves and differ in the length of the equilibrium period. The inherent structures are labeled as follows: E = -41.821 (■), -41.659 (●), -41.630 (▲), -41.588 (▼), -41.569 (♦) and > -41.569 kcal/mol (+). The inherent structures with energies of -41.821 and -41.659 kcal/mol are the global minimum and the second lowest energy minimum, respectively.
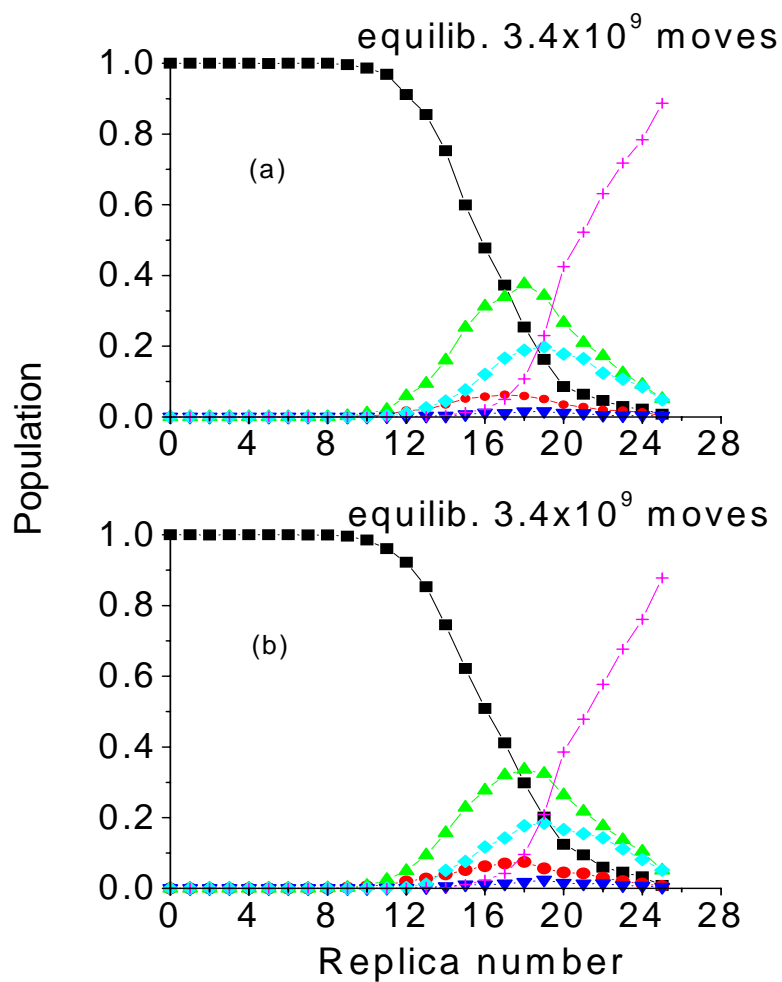
Figure 3.11 Inherent structure distributions from PTMC simulations of Ar_{38} starting from: (a) the global minimum and (b) the second lowest energy minimum. The simulations were carried out with an equilibration period of $3.4x10^9$ moves and production runs of $4x10^9$ moves. The inherent structures are labeled as follows: E = -41.821 (■), -41.659 (●), -41.630 (▲), -41.588 (▼), -41.569 (♦) and > -41.569 kcal/mol (+).
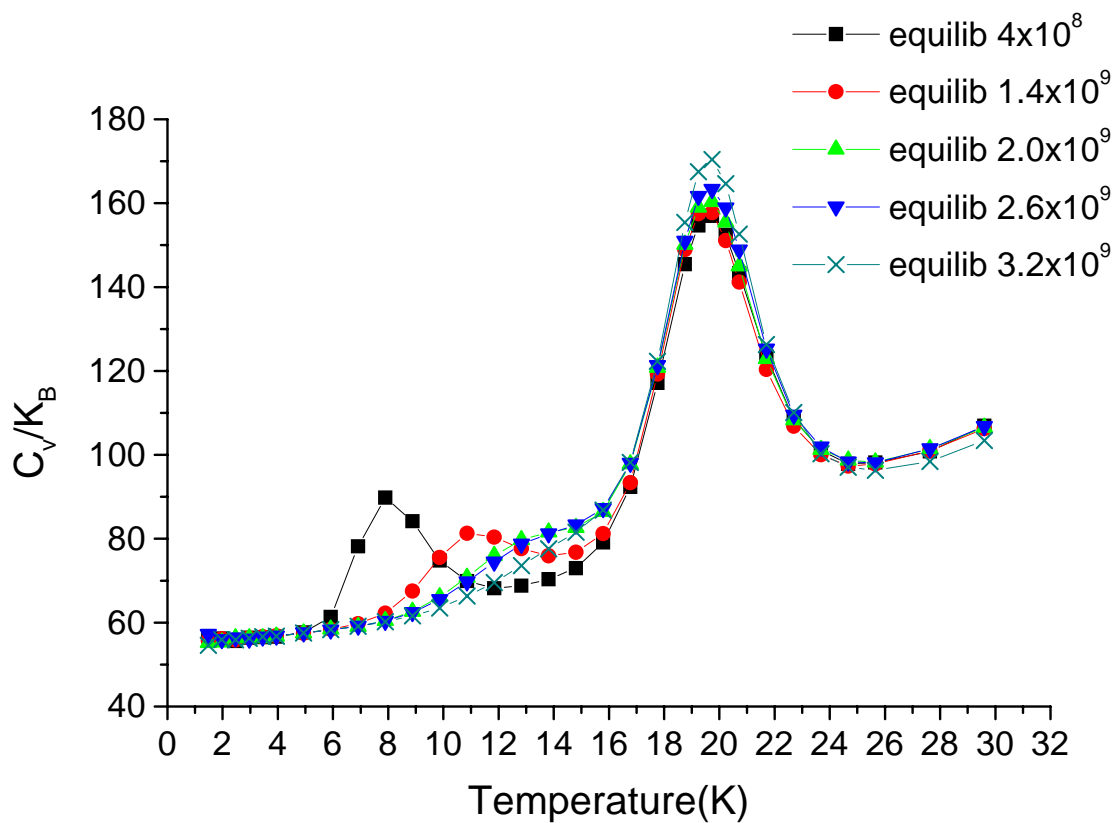
Figure 3.12 Heat capacity *vs.* *T* of Ar_{38} from PTTS simulations starting from the second lowest energy minimum. Equilibration periods ranged from 0.4×10^8 to 2.6×10^9 moves, and production periods were 1×10^9 moves for the case of an equilibration period of 0.4×10^8 moves and 0.6×10^9 moves in the other four cases.

4. Chapter 4 The application of Wang-Laudau free random walk algorithm on Ar cluster

4.1. Introduction

Simulations of systems with rough potential energy surfaces pose considerable challenges. Examples include high-density or low-temperature liquids, polymers, and proteins, for which the simulation is prone to be trapped in potential energy minima for large numbers of simulation steps. As mentioned in Chapter 1, numerous techniques have been proposed to overcome the quasi-ergodicity problem associated with rough landscapes and high energy barriers between energy minima. Techniques such as parallel tempering and multicanonical Monte Carlo have proven to be valuable. Multicanonical Monte Carlo simulations sample broad phase space by (ideally) using a uniform energy distribution. The trapping into energy minima can be artificially eliminated by assigning "weight" to different energy states. However the weight factors are not known so the multicanonical computation often requires tedious iterative calculations to get a good estimate of the weight factors.

As we have mentioned in Chapter 1, the Wang-Landau method directly and self-consistently determines the density of states by performing a random walk in the energy space. The WL algorithm has attracted a lot of attention, and it has been applied to biological systems and to quantum Monte Carlo calculations. The application of WL algorithm is very straightforward. The algorithm is also parallizable. Rathore *et al.*[104] have combined the WL algorithm and the parallel tempering scheme in their studies of the α-helix-coil and β-sheet-coil transitions of a designer peptide. Several new approaches[105,106] based on modifications of the WL algorithm have been published recently.

4.2. Method

The implementation of free random walk begins with a guess for the density of states, e.g., $g(E)=1$, initially for all states. $g(E)$ is improved by the following procedure:

1) Initialize conversion factor f_0 to a large number. In the original papers of Wang *et al.*[54,55] the value of the conversion factor was initially assigned as $e = 2.718$. Initialize all the density of states to 1.

2) Do Monte Carlo simulations, with trial Monte Carlo moves accepted with probability:

$$P_{i \to j} = \min(1, \frac{g(E_i)}{g(E_j)}) \qquad (4.1)$$

3) After each trial move, update the energy histogram and density of states. The density of states is updated by

$$g(E) = g(E) \cdot f \qquad (4.2)$$

If the move is accepted, the density of the accepted energy level is updated. Otherwise, the density of the old energy level is updated.

4) Check if the energy histogram is flat. If it is not flat, go back to 2). If it is flat, update the converter using $f_{i+1} = \sqrt{f_i}$, reset the energy histogram entries to zero, and start a new iteration of the free random walk in energy space.

5) Stop the simulation if f is close enough to 1.

Using the resulting density of states, the internal energy and heat capacity can be calculated by:

$$\langle E \rangle_T = \frac{\sum Eg(E)e^{-\beta E}}{\sum g(E)e^{-\beta E}} \qquad (4.3)$$

and

$$C(T) = \frac{<E^2> - <E>^2}{K_b T^2}. \qquad (4.4)$$

4.3. Simulation details

The WL free random walk algorithm was originally tested to investigate phase transition of the Ising model[54]. After that, a number of groups have applied this method to applications include protein,[107] polymer films.[108,109] Thus far there is no report of the application of the WL algorithm to investigate the thermodynamic properties of clusters.

One of the most intriguing aspects of this approach is that density of states can be used to obtain an estimate of the entropy. In this chapter, the WL free random walk algorithm is applied to the Ar_{13} and to the much more complicated Ar_{38} cluster.

The thermodynamic properties of Ar_{13} have been explored with a wide range of algorithms.[30,33,91] The system is defined by Lennard Jones interactions. In our simulations, a constraint sphere of 5 Å has been applied to the cluster. A single atom of Ar is chosen at random and moved to a new position. The maximum step size is 0.5 Å. The energy of the trial system is calculated and the probability of accepting the move is based on equation 4.1. The system is allowed to move in the energy range of -10.7 kcal/mol to 0 kcal/mol. A total 50 bins were used to divide up the energy range.

The free random walk algorithm was also applied to Ar_{38}. In this case the constraint sphere was chosen to be 8.5 Å. The energy range in the simulation is from -41.3 kcal/mol to -30 kcal/mol. The energy range was binned with a bin-size of 0.2 kcal/mol. For the Ar_{38} cluster it is difficult to get a flat energy distribution, at least when using single atom moves. Since the system is allowed to move freely in the energy space, the acceptance ratio is proportional to the density of states. If the energy of a newly generated configuration fills within an energy bin which has not been visited before, the move will definitely be accepted. However, randomly generating configurations at the low energies is much more difficult than at high energies, particularly for the systems

74

with sharp funnels in their potential energy surface. A second approach has been tested for updating configurations. A pivot (reflection point within the constraint sphere) was randomly chosen, then the atoms within the distance of 3.5 Å of the pivot are subject to a reflection with respect to the pivot. The group and reflection method for updating the configurations has been applied in the geometric cluster algorithms developed by Luijten *et al.*[110] Such multiple-moves are very useful in some cases since they keep the basic interactions within the group (e.g., in the water cluster, the reflection would retain hydrogen bonds within the group).

Even with the geometry group scheme to update the configurations, it is still not possible to get a flat energy distribution in the region of the global and second lowest energy minima. In the simulation of Ar_{38}, The energy range to do free random walk is -41.3 kcal/mol to -30 kcal/mol.

4.4. Results and discussion

Figure 4.1 compares the heat capacity curve of Ar_{13} calculated using WL algorithm and with jump walk Monte Carlo method. It has been established that jump walk algorithm is suitable for Ar_{13} system[33]. 16 temperatures were used in the jump-walk Monte Carlo simulations. Overall there is a fair agreement between the heat capacity curves calculated using the two approaches. WL simulations are much faster to converge and do not depend on the spacing of the temperature grid. Basically you can calculate any thermodynamic properties at any temperature in the free random walk algorithm.

However for Ar_{38} the heat capacity curve calculated using the free random walk procedure is only in fair agreement with the PTTS curve depicted earlier. Figure 4.2 compares the heat capacity curve of Ar_{38} calculated using WL algorithm and PTTS

method. The heat capacity shows a small bump at the temperature 15 K but the shape of

the heat capacity curve is not correct.
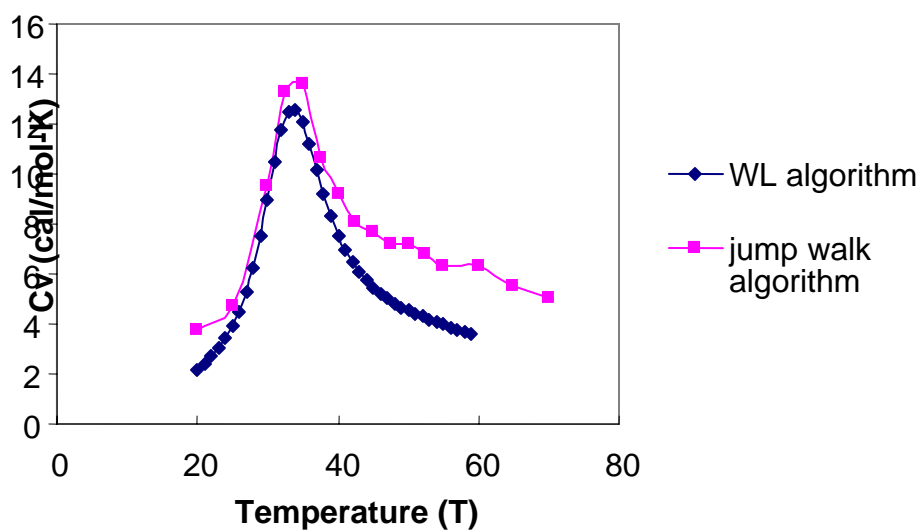
Figure 4.1 Heat capacity *vs.* temperature curves of the Ar_{13} cluster. The blue line denotes the result obtained using the WL algorithm, the purple line denotes results obtained using the jump walk algorithm.
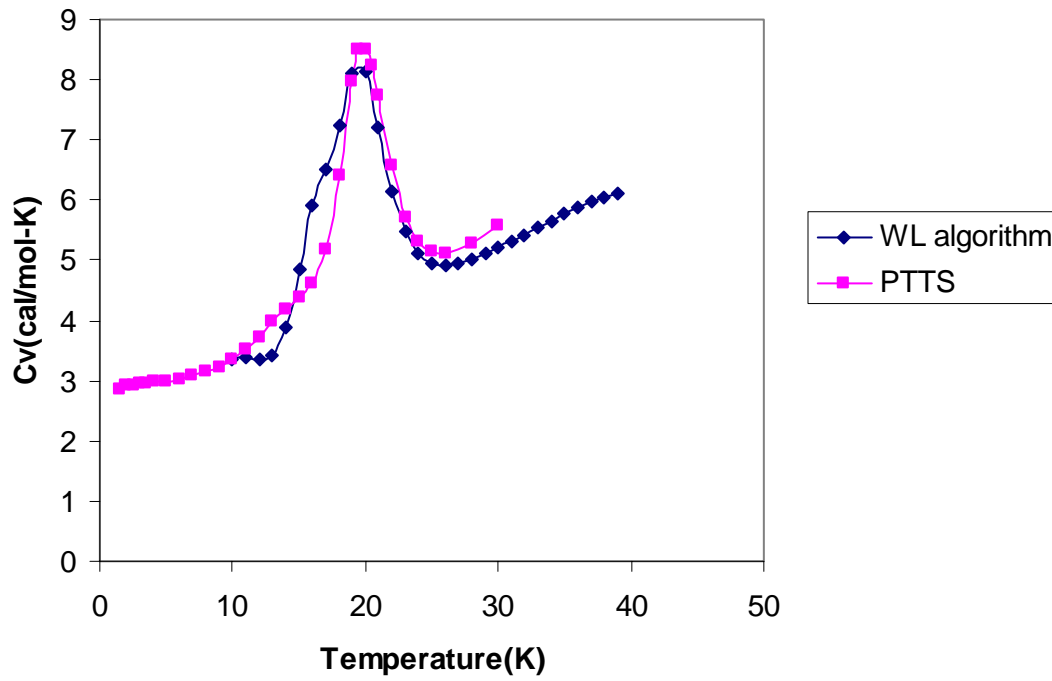
Figure 4.2 Heat capacity *vs.* temperature curve of Ar$_{38}$ obtained using the WL algorithm and PTTS algorithm.

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Appendix A

Computational study about the stereochemistry of the cyclization of a secondary alkyllithium

I. Introduction

Intramolecular carbolithiation has provided an efficient means for the construction of 5 or 6-membered carbocycles and their heterocyclic analogs.[1-3] The attraction of this methodology lies in the high stereo selectivity when carbon carbon bond is being formed and the possibility of trapping the resulting cyclized organolithium with various electrophiles to introduce diverse functionality into the cyclized products. It has been established that reductive lithiation of phenylthioether is a general method for the generation of organolithiums and an in depth study about its use in intramolecular carbolithiation has been reported[4]. Most interestingly, secondary alkyllithium cyclization (I, Scheme 1) is highly stereoselective with *trans* to *cis* ratios as high as of 40:1. Bailey observed similar trend but with lower yield in his study of the cyclization of the same secondary alkyllithium (I) generated from halogen–lithium exchange.[5] In examining the molecular model, the presumed transition state structure shown as III in Scheme 1 would lead to *cis* product. When the C-Li bond is parallel to the remote C=C double bond, the methyl has to locate in a pseudoaxial position, which will cause some steric problem with the vinyl hydrogen on inner carbon of the olefin. On the contrary, putting the methyl group on the pseudoequatorial position, which has no such steric effect as discussed above, would lead to the *cis* product (IV). Since the experimental results show that trans product is predominant one, it is of interesting to see the reasoning why trans product is formed instead of *cis* one. In his study of similar secondary alkylmagnesium cyclization,

Richey has proposed late transition state for his reaction to explain the high trans selectivity in his reaction (trans/cis=10:1 in his case).[6] However, it will be interested to the synthetic community by doing calculations to explain the high trans selectivity in our secondary alkyllithium cyclization. Since THF is used as the solvent for the reaction and THF is known to be lithiophilic, it will be of interesting to examine the solvent effect.

(I) (II) (III) (IV) ?
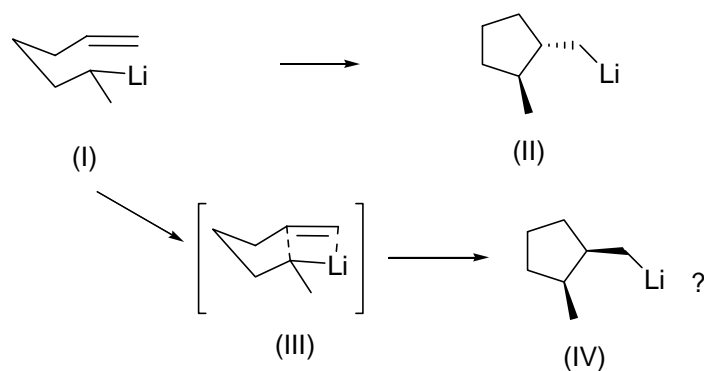
Scheme 1 Secondary alkyllithium Cyclization

II. Computational details

Calculations employing the B3LYP hybrid density functional method[7-9] were used to investigate the mechanisms of secondary cabanionic cyclization depicted in Scheme 1. Geometry optimization of all reactants, products and transition states were carried out using the 6-31+G(d) basis set[10]. Transition states were located using the synchronous transit-guided quasi-Newton method of Schegal (QST3). Harmonic frequency calculations were performed to establish the nature of each stationary point, to calculate vibrational zero-point energy corrections, and to estimate free energies at the reaction temperature -78 °C. All calculations were carried out using Gaussian 03[8].

The experiments were carried out in THF at -78 °C. Initially the solvent effect was included through the polarizable continuum model (PCM)[11,12]. However, it is very

likely under these experimental conditions the Li+ ion is coordinated by THF molecules. In order to investigate the importance of such coordination, calculations were also carried out with inclusion of one or two THF molecules. Reactants, products and transition states coordinated with one or two THF molecules are indicated by (thf)$_n$ (n=1, 2) in the figures and tables.

III. Result and Discussion

The optimized minima and transition states are depicted schematically in Figures 1-3. Detailed structural parameters and energies for all the structures are reported in the supporting information. The energies, ZPE's, and free energy corrections of reactants, transition states, and products are reported in tables 1-3.

The cyclohexane chair-like reactants are actually intermediates with the stability derived from interaction of the Li$^+$ with the π bond[13,14]. There are *cis* and *trans* coordinated complexes. The reaction is racemic so both *cis*- and *trans*-complexes contain mirror image structures. As can be seen from the data summarized in Figure 1, the energies of *cis* reactant and *trans* reactant are very close with the *cis*-complex calculated to be only 0.50 kcal/mol lower in energy. The greater stability of the *cis* complex appears to be due to the less steric effects. There are a number of short, non-bonded hydrogen-hydrogen and carbon-hydrogen interactions present in the *trans* intermediate complex caused by the pseudoaxial methyl group.

The *trans* product is predicted to be 3.0 kcal/mol more stable than the *cis* product as a consequence of steric effects of the cis product involving the methyl substituent and the –CH$_2$Li on the cyclopentane ring.

First, the theoretical study of gas phase pathways leading to cis and trans product are conducted. The transition state search gives a chair-like transition state for the *cis* reaction path. However, two transition states, one chair-like and the other twisted, are found to lead to the *trans* product. In the twisted transition state, the methyl group connected to C6 is in the equatorial plane, while in the chair-like transition state it is in the pseudoaxial position. The twisted transition state is calculated to be about 0.18 kcal/mol lower in energy than the chair-like transition state for the *trans* pathway. The transition state on the *cis* pathway is calculated to be 0.14 and 0.52 kcal/mol lower in energy than the *trans* (twisted) and *trans* (chair-like) transition states, respectively. Hence, the theoretical results for the gas phase pathways do not account for the highly *trans*/*cis* ratio (40:1) observed in the experiments.

The solvent effect was included by performing single point calculations on the optimized structures of the minima and transition states with PCM model of THF solvent. The results show almost no changes in the reaction activation energies and can't explain the experiment results either.

We now consider the results of the calculations including explicit THF molecules. Calculations about the effect of THF molecules on the reaction pathways are rare in the literature. Piffl *et al*[15] published their study on THF coordination with the sulfur-stabilized allyllithium compounds both in NMR study and theoretical calculations. Our study about the THF effect on the reaction pathways is shown in Figures 2 and 3, which depicted the optimized structures of the THF-containing complexes as well as the total energies with zero-point energy and free energy corrections. From these figures, it can be seen that the C2-Li and C6-Li distances increase as a result of the coordination of THF.

The coordination of THF with Li$^+$ weakens the interaction of Li with the π bond as well as the carbon-lithium bond. A single THF molecule cause a stabilization of the chair-like *trans* transition state relative to the twisted trans and *cis* transition states. In the chair-like *trans* transition state the two rings lie roughly in the same plane, minimizing the H-H non-bonded interactions. However, in the chair-like *cis* transition state and twisted *trans* transition state, the dihedral angles of the THF ring and the transition state ring are about 150°. This flipping up of THF ring is due to the existence of the equatorial methyl group connected to C5. With one THF molecule, the activation energy of the *trans* pathway is 2.65 kcal/mol below that in the *cis* pathway which would lead to over a 99% selectivity for the trans product, well matching the experimental results.

The net binding energy of two THFs with reactant complex is calculated to be about 18 kcal/mol. The energy of the *trans* reactant complex is now calculated to be 1.679 kcal/mol less stable than the *cis* complex. The activation energies of all three pathways for two THF molecules are greater compared with one THF. However at temperature -78°C, the ΔH for evaporation is -9.05 kcal/mol. It appears that the second THF would prefer to stay in the solvent rather than coordinate with Li$^+$. Probably it is rare for two THF molecules to coordinate with one Li$^+$ at the same time. So this reaction pathway will not be very likely happened in the real system.

IV. Conclusions

The lithiophilic solvent THF plays an important role in the high steroselectivity reaction of secondary alkyllithium cyclization. Steric effects have been shown to have a major influence on the selectivity of this reaction. Quantum mechanical calculations about the coordination of one THF molecule with Li$^+$ can be used to explain the

experimental results very well. THF is a principal member of the class of dipolar aprotic

solvent, which serves as ideal media for a variety of important chemical reactions. The

strong interaction of THF with Li^+ and the steric effect caused by THF is believed to

increase the selectivity of the cyclization reaction and even change the reaction pathway.

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	Cis-complex	Trans-complex	Cis-TS(chair)	Trans-TS(twist)	Trans-TS(chair)	Cis-prodcut	Trans-product
HF energy	-282.06134	-282.06084	-282.04964	-282.048355	-282.04857	-282.72592	-282.07551
Zero-point correction	0.18211	0.18231	0.18314	0.18228	0.18281	0.18478	0.18418
Sum of electronic and thermal Free Energies	-281.89888	-281.898085	-281.88539	-281.885175	-281.88474	-281.90703	-281.91108
detaG(kcal/mol)	8.464	8.101(twist) 8.369(chair)				5.113	8.152
deta(detaG)(/kcal/mol)	0.363					3.039	

Table 1 Calculated B3LYP/6-31+g(d) Energies of reaction is gas phase. (Structures are depicted in Figure 1)
The units of energy in the table are Hartree if not specified. 1H = 627.51 kcal/mol.

	Cis-complex-THF	Trans-complex-THF	Cis-TS(chair)-THF	trans-TS(twist)	Trans-TS(chair)-THF	Cis-product-THF	Trans-product-THF
HF energy	-514.547115	-514.546865	-514.53132	-514.53421	-514.53513	-514.56442	-514.56818
Zero-point correction	0.30104	0.30093	0.30128	0.30093	0.30134	0.30358	0.30321
Sum of electronic and thermal Free Energies	-514.271859	-514.271634	-514.255691	-514.25867	-514.25969	-514.28716	-514.29188
detaG(kcal/mol)	10.145	7.492 (chair) 8.135(twist)					
deta(detaG)(kcal/mol)	2.653						

Table 2 Calculated B3LYP/6-31+g(d) Energies of reaction with 1 THF. (Structures are depicted in Figure 2) The units of energy in the table are Hartree if not specified. 1H = 627.51 kcal/mol.

	Cis-complex-2THF	Trans-complex-2THF	Cis-TS(chair)-2THF	Trans-TS(twist)	Trans-TS(chair)-2THF	Cis-product-2THF	Trans-product-2THF
HF energy	-747.01897	-747.01768	-746.99930	-747.00212	-747.00701	-747.04213	-747.04602
Zero-point correction	0.41883	0.41896	0.41965	0.41912	0.41961	0.42174	0.42135
Sum of electronic and thermal Free Energies	-746.63247	-746.62980	-746.61069	-746.61407	-746.61914	-746.653445	-746.65820
detaG(kcal/mol)	13.672	6.685(chair) 9.867(Twist)					
Deta(detaG)(kcal/mol)	6.987						

Table 3 Calculated B3LYP/6-31+g(d) Energies of reaction with 2 THF. (Structures are depicted in Figure 3) The units of energy in the table are Hartree if not specified. 1H = 627.51 kcal/mol

cis-complex
(0.0)

cis TS (chair-like)
(8.464)

cis-product
(-5.113)

trans-complex
(0.499)

trans TS (chair-like)
(8.875)

trans TS (twist)
(8.606)

trans product
(-7.652)
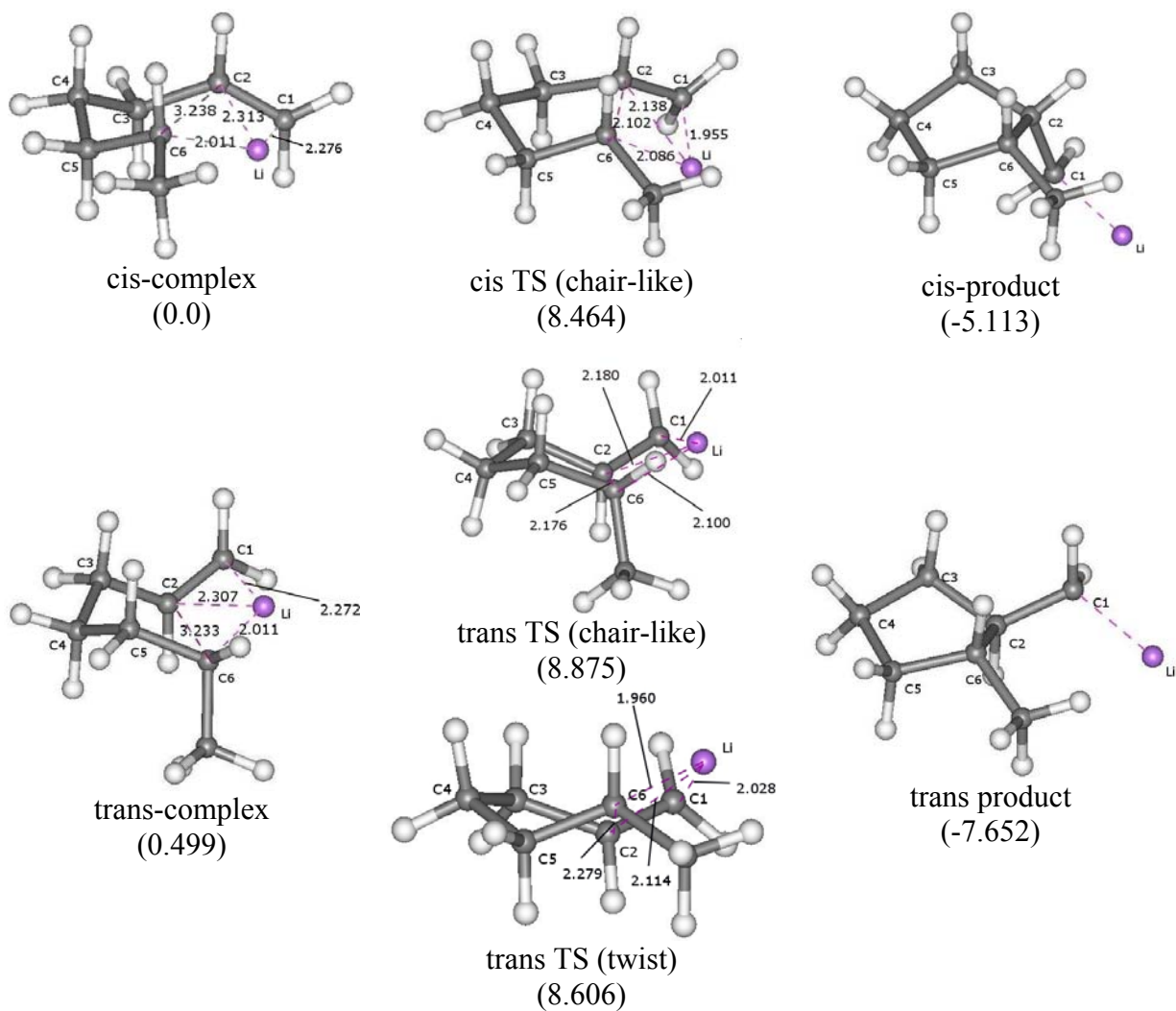
Figure 1 Calculated reaction paths. The numbers within () denote the relative energy in kcal/mol.

cis-complex with 1THF
(0.0)

cis TS with THF (chair-like)
(10.145)

cis-product-with 1THF
(-9.603)

trans TS with THF(chair-like)
(7.639)

trans-complex with 1THF
(0.141)

trans-product with 1THF
(-12.563)

trans TS with THF(twist)
(8.2743)

Figure 2 Calculated reaction paths with 1 explicit THF molecule. The numbers within ( ) denote the relative energy in kcal/mol

cis-complex with 2THF
(0.0)

cis TS with 2THF(chair)
(13.672)

cis product
(-13.160)

trans-complex with 2THF
(1.679)

trans TS with 2THF(chair)
(8.365)

trans TS with 2THF(twist)
(11.546)

trans product
(-16.143)
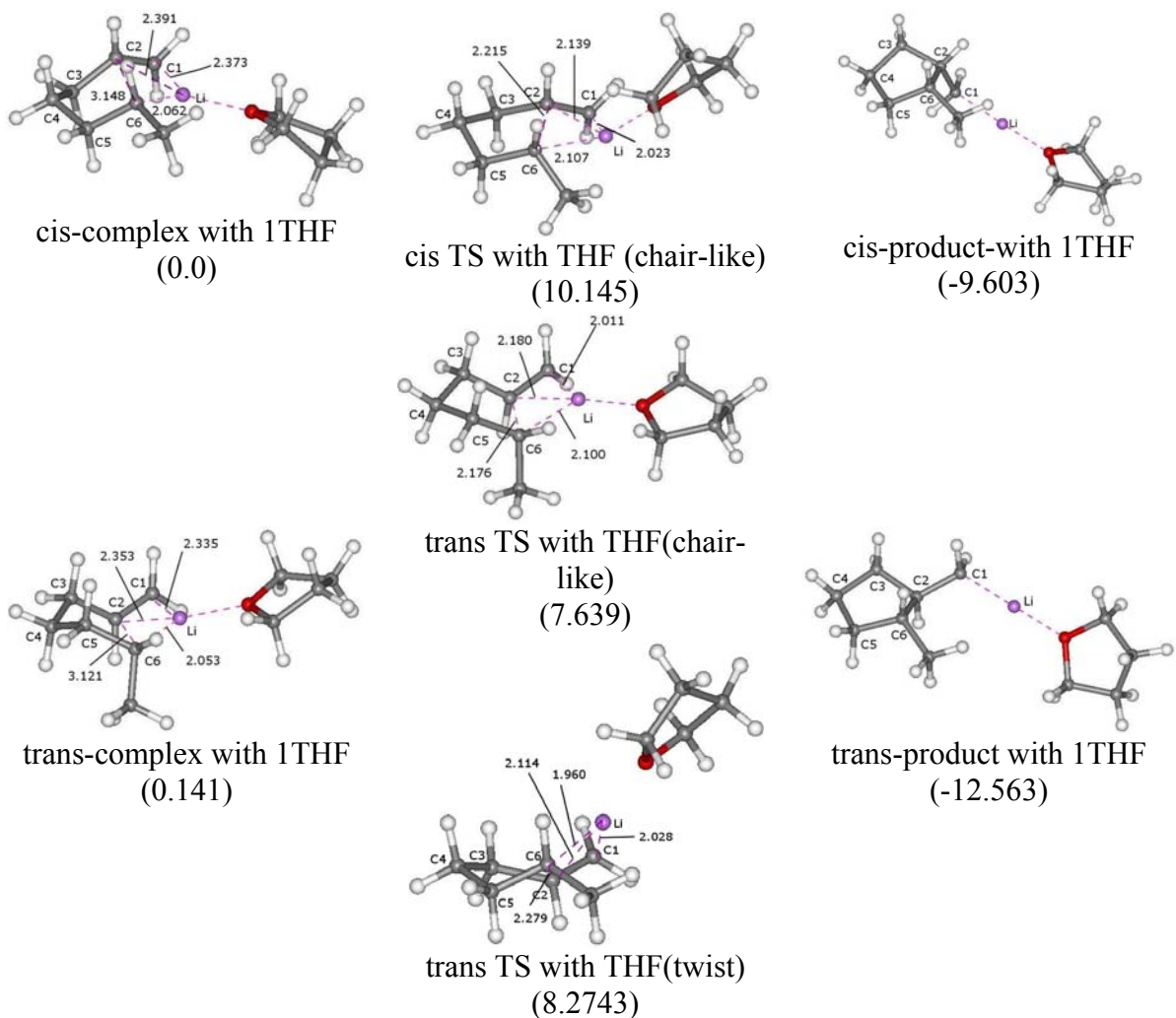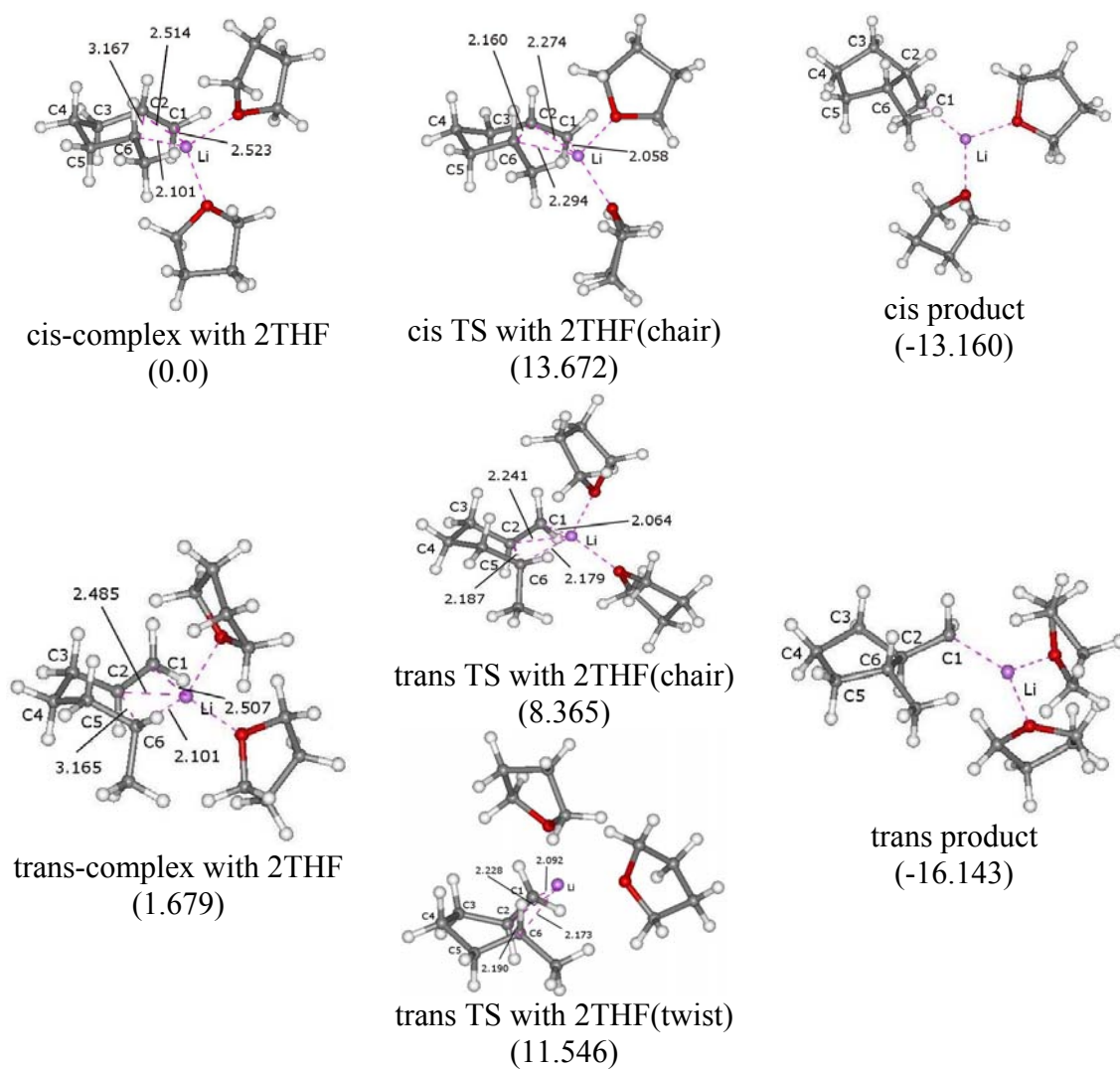
Figure 3 Calculated reaction paths with two explicit THF molecules. The numbers within () denote the relative energy in kcal/mol.

Appendix B

Theoretical characterization of the $(H_2O)_{21}$ cluster

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Abstract: In this paper, we examine theoretically the structures and energies of selected low energy isomers of $(H_2O)_{20}$ and $(H_2O)_{21}$, with particular attention paid to isomers derived from water dodecahedron. Results are reported for the Becke3LYP density functional and the RI-MP2 electronic structure methods, as well as for several water models. The calculations reveal that the global minimum structure of $(H_2O)_{21}$ is a water dodecahedron with an interior water molecule engaged in four hydrogen bonds. This indicates that the excess proton is not "driving" the high stability of the magic number $H^+(H_2O)_{21}$ cluster, the global minimum of which is also derived from the water dodecahedron and has interior water molecule.

I. Introduction

   Over the past few years, major strides have been made in understanding of the structure and dynamics of water clusters. Recently, there has been renewed interest in the $H^+(H_2O)_{21}$ cluster,[1-5] which appears as a magic number in the mass spectra of $H^+(H_2O)_n$ clusters[6-9] over three decades ago. Searcy and Fenn proposed that the $n = 21$ protonated cluster has a structure corresponding to a water dodecahedron with an enclosed water monomer and the excess proton on the surface.[6] Wei and Castleman, on the basis of a titration experiment, offered an alternative interpretation, namely that the $H^+(H_2O)_{21}$ cluster is comprised of a water dodecahedron with an interior H_3O^+ ion.[7] Recently it has become possible to determine the vibrational spectrum of the $H^+(H_2O)_{21}$ cluster by means of vibrational predissociation spectroscopy. Comparison of the measured spectrum, with the calculated spectra of various isomers, leads to the conclusion that the experimentally observed isomer is that originally proposed by Searcy and Fenn.[1-3] Moreover the calculations indicate that the Searcy-Fenn isomer is the global minimum of $H^+(H_2O)_{21}$.[1,4,5]

   For the neutral $(H_2O)_{20}$ cluster, the most stable dodecahedral isomer lies about 10 kcal/mol above the global minimum isomer which has a pentagonal prism (PP) structure.[10,11] This would seem to suggest that the presence of the proton is the key to the special stability of the dodecahedrally-derived global minimum isomer of $H^+(H_2O)_{21}$. However, there is experimental data that suggests that the neutral $(H_2O)_{21}$ cluster itself is especially stable. Specifically, Lee and Beauchamp observed a magic number at $n = 21$ for the tetrabutylammonium$(H_2O)_n^+$ cluster.[12] Since the charge in this mixed cluster is associated with the amine, this suggests that the water molecules are present as an $(H_2O)_{21}$ cluster with especially high stability. Although $H^+(H_2O)_{21}$ and $(H_2O)_{20}$ have been

the subject of numerous theoretical studies, the neutral $(H_2O)_{21}$ cluster has received much less attention. Wales and Hodges have characterized $(H_2O)_{21}$ using the TIP4P water model[13] and reported that the global minimum has a "flat" structure comprised of fused four- and five- membered rings,[10] and hereafter referred to as TIP4P-gm(21).

In this paper, we examine theoretically the structures and energies of selected low energy isomers of $(H_2O)_{20}$ and $(H_2O)_{21}$, with particular attention paid to isomers derived from water dodecahedron. Results are reported for the Becke3LYP density functional[14-16] and the resolvent of the identity second order Møller-Plesset perturbation Theory (RI-MP2) electronic structure methods,[17] as well as for the TIP4P effective two-body model potential, and for the Dang-Chang,[18] AMOEBA,[19] and TTM2-F[20] polarizable water models.

II. Computational details

The Becke3LYP calculations were performed with both the 6-31+G(d) and aug-cc-pVDZ[21,22] basis sets, and the RI-MP2 calculations were performed using both the aug-cc-pVDZ and aug-cc-pVTZ(-f)[21,22] basis sets. The –f in the latter case indicates that the f functions on the O atoms and the d functions on the H atoms that would be present in the full aug-cc-pVTZ basis set have been omitted. The RI-MP2 calculations with the aug-cc-pVTZ(-f) basis set were carried out using the RI-MP2/aug-cc-pVDZ optimized geometries. The Becke3LYP and RI-MP2 calculations were carried out using Gaussian 03[16] and Turbomole,[23,24] respectively. The calculations with the TIP4P and Dang-Chang, AMOEBA force fields were carried out using the Tinker program,[19,25-27] and the calculations with the TTM2-F force field were carried out using the Occident program from Xantheas group.[20]

Clusters of the size of $(H_2O)_{20}$ and $(H_2O)_{21}$ have a very large number of low-lying local minima, making location of the global minimum especially challenging.[10] In this work we adopted several strategies in searching for low energy minima. First, we selected low-energy structures from the Cambridge Cluster Database[10] which were located by means of the basin hopping Monte Carlo procedure[28] and using the TIP4P water model. In the case of $(H_2O)_{21}$, we also built structures by adding a water molecule in the interior of the $(H_2O)_{20}$ dodecahedron. Since there are multiple isomers of this type, these structures were used to initialize eigenmode-following searches[29-31] for other minima and as initial structures for use in simulated annealing calculations, carried out with molecular dynamics simulations and the AMOEBA force field. For $(H_2O)_{20}$, we also examined structures formed by removing one of the surface water molecule from the most stable dodecahedrally derived form of $(H_2O)_{21}$. The lowest energy structures thus located were used to initiate geometry optimizations with the various force fields as well as with the Becke3LYP and RI-MP2 electronic structure methods.

III. Results and Discussion

In discussing the results for $(H_2O)_{21}$, we focus primarily on the two isomers denoted TIP4P-gm(21) and DD(20,1) and depicted in Figure 1. The former is the global minimum located by Wales and Hodges using the TIP4P model, and the latter denotes a distorted dodecahedron with an interior water molecule engaged in four hydrogen bonds. The DD(20,1) isomer has a structure similar to the global minimum of $(H_2O)_{21}$ except for the absence of the excess proton in $H^+(H_2O)_{21}$. Figure 2 reports for the TIP4P-gm(21) and DD(20,1) isomers of $(H_2O)_{21}$ as well as of four forms of $(H_2O)_{20}$ the binding energies. The Becke3LYP/aug-cc-pVDZ and RI-MP2/aug-cc-pVDZ calculations place the

DD(20,1) isomer energetically below the TIP4P-gm(21) isomer by 6.7 and 4.2 kcal/mol, respectively. The energy difference between the two isomers is 4.6 kcal/mol at the RI-MP2/aug-cc-pVTZ(-f) level. Inclusion of corrections for vibrational zero-point energy (estimated at the Becke3LYP/6-31+G(d) level) further stablizes the DD(20,1) structure over the TIP4P-gm(21) isomer by 1.2 kcal/mol.

At the RI-MP2/aug-cc-pVDZ level of theory the counterpoise correction for basis set superposition error (BSSE) is 43.1 kcal/mol for both the DD(20,1) and TIP4P-gm(21) isomers. The corresponding counterpoise corrections are -28.1 and -27.5 kcal/mol at the RI-MP2/aug-cc-PVTZ(-f) level. Thus, while the BSSE corrections are large for the basis sets employed, they are nearly identical for the two isomers, for both basis sets considered. As a result, we conclude that the DD(20,1) isomer would be about 5 kcal/mol more stable (before ZPE correction) than the TIP4P-gm(21) isomer in the complete basis set limit.

The TTM2-F and AMOEBA polarizable models favor the DD(20,1) isomer by 1.1 and 4.0 kcal/mol respectively. On the other hand, the TIP4P and DC models both predict the TIP4P-gm(21) isomer to be slightly more stable than the DD(20,1) isomer. Thus, it appears that in a model potential approach both distributed polarizable sites and a realistic description of the electrostatics are required in order to properly describe the energy difference between the TIP4P-gm(21) and DD(20,1) isomers of $(H_2O)_{21}$.

For $(H_2O)_{20}$, results are reported in Figure 2 for the "perfect" dodecahedron [PD(20)], the pentagonal prism [PP(20)], and the DD(19,1) isomer, which is formed by removing a water from the surface of DD(20,1) and allowing for geometrical relaxation. The structures of the PD(20), PP(20), and DD(19,1) isomers are depicted on Figure 1. Figure

2 also reports energies for a structure designated DD(20,0), formed by removing the interior water molecule from DD(20,1), without allowing relaxation of the geometry. As seen from Figure 2, for $(H_2O)_{20}$, PP(20) is the global minimum at all levels of theory considered, although the energy gap between PP(20) and DD(19,1) is only 1.3 kcal/mol at the RI-MP2/aug-cc-pVTZ(-f) level. The DD(20,0) species is calculated to be less stable by 5-15 kcal/mol, depending on the theoretical method employed, than the PD(20) isomer. This represents the energetic cost of distorting the $(H_2O)_{20}$ dodecahedron into the structure it has in the DD(20,1) isomer. The DD(20,1) species is 26-35 kcal/mol more stable than the DD(20,0) species, for the theoretical methods considered. Again, the energy difference obtained using the TTM2-F and AMOEBA models are in fairly good agreement with the RI-MP2/aug-cc-pVTZ(-f) results.

There are siginificant differences between the relative energies, and those from the AMOEBA and RI-MP2 calculations. This may be a consequence of the well-known inadequency of the density functional methods for describing dispersion interactions.[32]

IV. Conclusions

The present study provides evidence that the DD(20,1) isomer of $(H_2O)_{21}$, which consists of a distorted water dodecahedron with an interior water engaged in four H-bonds, is significantly more stable than the TIP4P-gm(21) isomer, which is lowest energy isomer of $(H_2O)_{21}$ located with the TIP4P water model. At the RI-MP2/aug-cc-pVTZ(-f) level the DD(20,1) isomer is calculated to be 22.9 kcal/mol more stable than the global minimum of $(H_2O)_{20}$. This is an unusually large difference in stability for two adjacent (*i.e.*, *n* and *n+1*) water clusters and is consistent with the experiments of Lee *et al.*, which suggested an unusually high stability of $(H_2O)_{21}$. The high stability of the DD(20,1)

isomer derives from the presence of the four strong H-bonds involving the interior water molecule. These results also indicate that the high stability of the Searcy-Fenn form of $H^+(H_2O)_{21}$ is due primarily to the strong H-bonds involving the interior water monomer rather than to the excess proton.

Surprisingly, it is found that Dang-Chang polarizable water model fails to predict that DD(20,1) isomer is more stable than TIP4P-gm(21). The TTM2-F and AMOEBA water models, which employ distributed polarizable sites, do predict the DD(20,1) isomer to be more stable than the TIP4P-gm(21) isomer. Of these two models, the AMOEBA model, which also employs distributed multipoles, gives an energy difference closer to the RI-MP2 results than does the TTM2-F model. Thus it appears that the use of both distributed multipoles and distributed polarizable sites is necessary to provide a realistic description of $(H_2O)_{21}$.

For $(H_2O)_{20}$ the RI-MP2 calculations predict that the DD(19, 1) isomer to be only 1.3 kcal/mol less stable than the PP(20) global minimum isomer. Interestingly, several papers, discussing various type of isomers of $(H_2O)_{20}$, have not mentioned this species.[11,33,34]

The DD(20,1) isomer investigated here is calculated to have a dipole moment of 3.00 D. As a result, this isomer should form a stable dipole bound anion, which would allow access to the neutral DD(20,1) form of $(H_2O)_{21}$ via photo-detachment of the anion.

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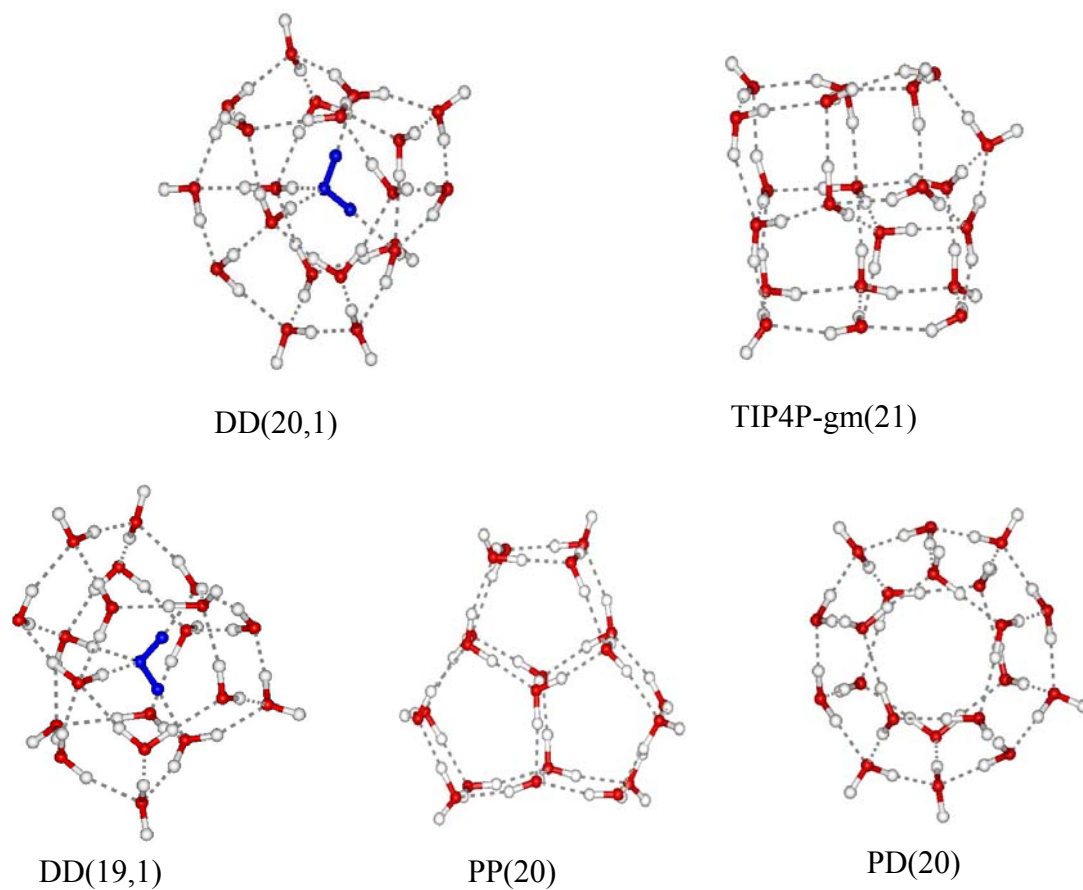DD(20,1)

TIP4P-gm(21)

DD(19,1)

PP(20)

PD(20)

Figure 1 RI-MP2/aug-cc-pVDZ optimized geometries of the DD(20,1) and TIP4P-gm(21) isomers of $(H_2O)_{21}$ and of the D(19,1), pentagonal prism [PP(20)], and "perfect" dodecahedron [PD(20)] isomers of $(H_2O)_{20}$.
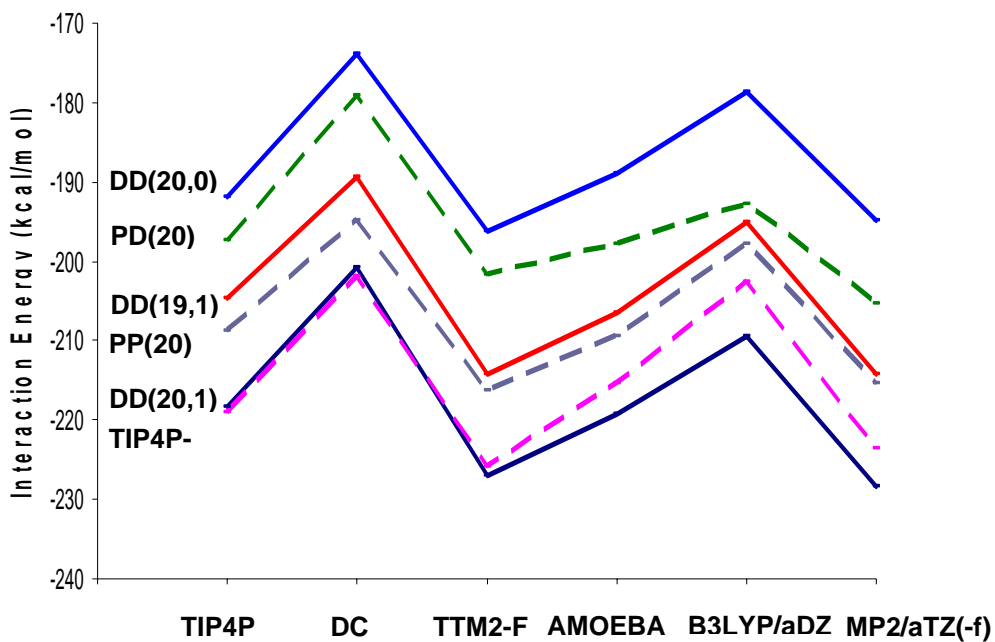
Figure 2 Interaction energies for the DD(20,0), PD(20), DD(19,1), PP(20), DD(20,1), TIP4P-gm(21) isomers at the TIP4P, DC, TTM2-F, AMOEBA, B3LYP/aug-cc-PVDZ, and RI_MP2/aug-cc-PVTZ(-f) levels of theory. B3LYP/aDZ refers to B3LYP/aug-cc-pVDZ Calculations. MP2/aTZ(-f) refers to RI-MP2/aug-cc-pVTZ(-f) calculations.