# An Effective Transition State for a Complex Cluster Isomerization Process: comparison between anharmonic and harmonic models for $Mg^+Ar_{12}$

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# Abstract

The isomerization reaction between two discernible categories of structures of $Mg^+Ar_{12}$ with the magnesium cation inside the argon cluster (solvated), and on the surface of the argon cluster (non-solvated), discovered recently, is studied by computing the density of states with microcanonical and canonical Molecular Dynamics techniques. Thermodynamical properties and equilibrium constants are then evaluated after establishing the validity of a single effective transition state. A complex kinetic model based on the Transition State Theory and the harmonic approximation is also developed to calculate thermodynamical properties, and isomerization rate and equilibrium constants. This model includes tens of intermediate minima and transition states located on the potential energy surface of the cluster. The general good agreement between the two models is encouraging for studying complex isomerization processes in atomic clusters with simplified theories.

## I. Introduction

The isomerization reaction between two isomers separated by a single transition state is one of the elementary chemical processes which can occur in small polyatomic molecules. In larger systems, isomerization may involve complex schemes because of the large number of possible intermediate isomers, and, the even larger number of possible paths to move from one isomer of importance to another.

The first step to understand isomerization in chemical systems is through the visualization of the morphology of the potential energy surface. The isomers correspond to minima on the potential function and the transition states are related to saddle points. In the frame of classical Transition State Theory (TST),[1] isomerization happens every time a trajectory initiated in the region of one isomer crosses the transition state to pass to the region of the other isomer. The transition state is usually defined as a hyperplane at the top of the barrier across the reaction path, but of course, several variants of the original TST have been proposed.[2] Statistical theories, such as TST, have successfully been applied to simple (elementary) isomerization processes. However, the extension of these models to complex isomerization reactions, which involve hundreds of intermediate minima and transition states, remains a difficult problem for theoretical chemistry.

A system for which a complex isomerization reaction has been found is the $Mg^+Ar_{12}$ cluster. Argon clusters doped with metal cations have recently been produced in a supersonic jet of argon connected to a laser vaporization source.[3] From the analysis of mass spectra the investigators were able to determine the most stable aggregates (magic numbers). The $Mg^+Ar_n$ case was carefully examined and higher intensity peaks (relative to the neighboring ones) were found for $n$=12,18,22,25,28, 31,45, and 54. These magic numbers of the cation clusters appeared to coincide with those of pure argon, and that led to the speculation that the geometry of $Mg^+Ar_{12}$ was the same with that of $Ar_{13}^+$, i.e., a regular icosahedron.[4]

To further study and confirm the conclusions of this experimental work, we have investigated with Molecular Dynamics techniques the equilibrium structures and dynamics of small $Mg^+Ar_n$ and $Mg^{++}Ar_n$ aggregates.[5] We indeed found that the icosahedral geometry of $Mg^+Ar_{12}$ is the most stable, but, we also showed that two almost isoenergetic icosahedral structures exist. One with $Mg^+$ *in the center* of the icosahedron, and one with the cation *on the surface* of the cluster. Such findings immediately raise the questions about the thermodynamic stability of the two isomers, and the mechanism of isomerization. To answer such questions it is necessary, first, to locate the intermediate minima and saddle points of the potential function, and second, to evaluate isomerization rates among these minima.

It turns out, that $Mg^+Ar_n$ clusters may serve as good model systems for experimental[3,6] and theoretical studies of metal-ion doped clusters. Therefore, we have further pursued the study of $Mg^+Ar_{12}$ by locating a large number of stationary points of the potential energy surface using modern unconstrained optimization algorithms.[7] One way to display the stationary points in a mode that unveils topographical characteristics of the potential energy surface is by plotting their energies as a function of an effective reaction coordinate. In the case of $Mg^+Ar_{12}$ the distance of $Mg^+$ from the center of mass of the cluster is defined as the isomerization coordinate. We name such plots *stationary point diagrams*, and they give the distribution of the minima and transition states along the reaction path.[7]

*Stationary point diagrams* can be used to draw qualitative conclusions about the isomerization processes. However, if we demand the reaction rates, then, we must calculate the rate constants of all intermediate steps, a difficult task when hundreds of intermediate isomers are involved. Thus, simplified theories are required, and the purpose of this article is to introduce and test two simple models for the calculation of the density of states (DOS) as a function of the total energy, and from this to estimate thermodynamical functions, and rate and equilibrium constants of the isomerization reactions.

In the first model, we test the assumption of the existence of a single effective transition state which separates the configuration space into two regions. In this way, we reduce the complex isomerization reaction to an elementary one. However, we accurately compute the densities of states for the full anharmonic potential with canonical,[8,9] and microcanonical Molecular Dynamics methods.[10]

In the second model, we use all the located intermediate minima and isomerization reactions among them to represent the complex isomerization scheme, but, we reduce the computational cost which is required for the accurate evaluation of the probabilities to move from one minimum to the other, by introducing the TST and the harmonic approximation.[11] These two models are applied to study the isomerization reaction between the two icosahedral geometries of $Mg^+Ar_{12}$.

The article is organized as follows. After this introduction (Section 1), we briefly present in Section 2 the potential function, we develop in Section 3 the two theoretical models, Section 4 gives the results, and Section 5 their discussion. Finally, we summarize in Section 6 the main conclusions of the present study.

## II. Potential Function and its Morphology

The interaction potential of $Mg^+Ar_n$ clusters is written as[5]

$$V_{tot} \;=\; \sum_{k=2}^{n+1} V_n^+(1,k) \;\;+\;\; \sum_{j=2}^{n}\sum_{k=j+1}^{n+1} V_{nn}(j,k). \tag{1}$$

The first sum describes the interactions of Mg ion (labeled as atom 1) with the atoms of argon (labeled as atoms 2,3,...,$n+1$). The second term in Eq. (1) denotes the interactions among argon atoms. $V_n^+(1,k)$ is an electrostatic potential which includes the charge – induced dipole and induced – dipole induced – dipole interactions. The repulsive part of the potential and the dispersion forces are described by a Morse type function. The parameters introduced in the potential are fitted by using the results of ab initio calculations.[12,13] A detailed description of the potential function is given in ref. [5]. We must point out that, although the potential is written as a sum over all pair atom contributions, many-body terms are included through an iterative way to compute the induced dipole moment of each atom at the current positions of all other atoms.

Using mainly the damped–Broyden-Fletcher-Goldfarb-Shanno (BFGS) method[14] we have located 83 minima and 137 related saddle points of $Mg^+Ar_{12}$ in the energy range of about 2.5 kcal/mol above the absolute minimum. After that, following the steepest descent directions we have found the ways minima and transition states are connected. Initial conditions for the minimization are selected with two methods. A systematic one by deforming the cluster from a known equilibrium geometry, and a random one by choosing an initial point in the configuration space with an arbitrary arrangement of the atoms. The second method usually gives high energy initial structures. In spite of that, the most frequent endings of the minimization processes were the stationary points located at low energies, in the range of 2.5 kcal/mol above the absolute minimum.

The most stable minima are the two highly symmetric icosahedral structures, one with the magnesium cation in the center of the icosahedron, that we call isomer $(a)$ ($iso\ (a)$), and the other with the cation on the surface, that we call isomer $(b)$ ($iso\ (b)$) (Fig. 1). In the previous article[5] we have shown, that the absolute energy minimum is obtained for $iso\ (b)$ (-23.589 kcal/mol) with an energy lower than that of $iso\ (a)$, by 0.5 kcal/mol ($E = -23.056$ kcal/mol). The reference energy ($E = 0$) corresponds to a configuration with all atoms separated.

In Fig. 2 we have represented the distribution of the minima (filled squares) and transition states (open circles) by plotting their potential energy as a function of the distance of magnesium cation from the center of mass of the cluster, $R_{Mg^+-c.m.}$. Hence, $iso\ (a)$ corresponds to $R_{Mg^+-c.m.} = 0\ a_o$, and $iso\ (b)$ to 5.41 $a_o$. Stationary points with a non–solvated magnesium can reach configurations with $R_{Mg^+-c.m.}$ up to 6.5 $a_o$. The variable $R_{Mg^+-c.m.}$ may be considered as an effective reaction coordinate which describes the isomerization process

$$iso\ (a) \longleftrightarrow iso\ (b). \tag{2}$$

The *stationary point diagram* shown in Fig. 2 can provide useful information about the mechanism of the isomerization processes in the cluster. Indeed, we immediately note that the highly symmetric conformations, $iso\ (a)$ and $iso\ (b)$, have an enhanced stability because of the energy gaps that separate these two minima from the other relative minima. We can also remark that the density of stationary points in the vicinity of $iso\ (b)$ is higher than in the vicinity of $iso\ (a)$. This means that the cluster will be trapped for long times in this region of configuration space. However, to obtain estimates of the isomerization times for Eq. (2) dynamical models must be developed, and this is done in the next section.

# III. Theory and Computational Details

In this paper, we have been mainly interested in the dynamical behavior of the strongly anharmonic $Mg^{+}Ar_{12}$ cluster. More specifically, we wanted to analyze the relationship between dynamics in the microcanonical ensemble and the structure of the phase space through its density of states. The dynamical behavior has been studied from the analysis of trajectories in the phase space.

## A. Characterization of the microcanonical dynamics

The atomic aggregate is described in a space-fixed cartesian coordinate system. A variable order, variable time step algorithm[15] is used to integrate the Hamilton equations of motion. During the integration several quantities are computed which characterize the thermodynamical and dynamical properties of the system. Such quantities are: the caloric curve, i.e., the average kinetic energy as a function of the total energy, $E$, root mean square fluctuations of the bond lengths from the average values,

$$\delta_{Ar-Ar} = \frac{2}{n(n-1)} \sum_{i=2}^{n} \sum_{j>i}^{n+1} \frac{\sqrt{< r_{ij}^2 > - < r_{ij} >^2}}{< r_{ij} >}, \tag{3}$$

where $r_{ij}$ is the distance between the $i^{th}$ and the $j^{th}$ Ar atom.

To obtain the average quantities we integrate one trajectory at total energy $E$ for times up to 15 ns. The energy of the system is increased by scaling the momenta and always keeping the total angular momentum equal to zero. After initializing a trajectory, we let the system equilibrate by integrating the equations of motion for 1 ns at low energies up to 5 ns at higher energies, before we start selecting points for the evaluation of the average values.

In spite of these long equilibration times, it was found that the isomerization process was very slow, even when the total energy was set to a few kcals/mol above the first observed transition between *iso* $(a)$ to *iso* $(b)$. Hence, it is difficult to assure that one trajectory can efficiently sample the phase space above the isomerization barrier. Therefore, several trajectories were run, initiated either from the region of minimum $(a)$ or from that of minimum $(b)$.

Since, we were interested in the isomerization process between solvated and non-solvated isomers, we have searched for a coordinate which could characterize the transition state that separates these two regions of the configuration space. As is shown in the next section, the distance between the cation and the center of mass of the cluster, ($R_{Mg^+-c.m.}$), can distinguish the two families of isomers.

## B. Density of states

For the calculation of the exact microcanonical density of states, two different approaches have been used. The first method was based on the properties of the probability distribution in the canonical ensemble.[16–18] At constant temperature, the normalized probability to obtain the total energy between $E$ and $E + \Delta E$ is linked to the microcanonical density of states $\omega(E)$ by :

$$P_T(E) = \frac{\omega(E)\Delta E \; e^{-\beta E}}{Z(\beta)}, \tag{4}$$

where $Z(\beta)$ is the canonical partition function, and $\beta = 1/kT$, ($k$ is the Boltzmann constant). This relationship can be discretized over a grid of energies $E_i$ and temperatures $T_j$. Thus, at a given temperature $\beta_j$ the probability to obtain the total energy $E_i$ can then be expressed as :

$$P_{ij} = \frac{\rho_i \; e^{-\beta_j E_i}}{Z_j}, \tag{5}$$

where $\rho_i = \omega_i \Delta E$.

It follows that if canonical simulations are run for $M$ different temperatures in order to obtain a set of $M$ normalized probability curves, the multiple histogram method, as described by Weerasinghe and Amar,[17] can be used for the extraction of the exact anharmonic microcanonical density of states. Such canonical simulations were obtained by running Nosé dynamics trajectories[8,9] for the total angular momentum $\vec{J} = \vec{0}$. The scaling of the $\omega(E)$ function was then adjusted by fitting it at low internal energies to the harmonic curve, which is completely defined by the knowledge of the harmonic frequencies at the equilibrium configuration.

The canonical partition function can then be deduced by :

$$Z(\beta) = \int_0^\infty \omega(E) e^{-\beta E} dE. \tag{6}$$

The second approach is based on the properties of phase space in the microcanonical ensemble following the theoretical scheme recently proposed by Calvo and Labastie.[10] In the microcanonical ensemble, the normalized probability to find the potential energy between $V$ and $V+\Delta V$ is given by :

$$P_E(V) = \frac{\omega^k(K)\Delta K\, \omega^c(V)\Delta V}{\omega(E)\Delta E}, \tag{7}$$

where $\omega^k(K)$, $\omega^c(V)$, and $\omega(E)$ are the kinetic, configurational, and microcanonical densities of states, respectively. It can be shown that the kinetic density of states is given by the following analytic expression :

$$\omega^k(K) = AK^{\frac{3n_a-8}{2}}, \tag{8}$$

where $A$ is a constant factor and $n_a$ $(= n+1)$ the number of atoms in the cluster.

From Eqs (7) and (8), we can write a discretized form of $P_E$ :

$$P_{ij} = \frac{A(E_i - V_j)^{\frac{3n_a-8}{2}}\rho_j^c}{\rho_i}, \tag{9}$$

with $\rho_i = \omega_i \Delta E$ and $\rho_j^c = \omega_j^c \Delta V$. Molecular Dynamics simulations at constant energy were run for a set of $M$ different internal energies. Consequently, the configurational density of states $\omega^c(V)$ could be extracted with the multiple histogram method. The total density of states $\omega(E)$ was then easily obtained by :

$$\omega(E) = \int_0^E AK^{\frac{3n_a-8}{2}}\omega^c(E-K)dK. \tag{10}$$

As in the previous case, the density of states were fitted at low internal energies to the harmonic density of states.

At high excitation energies a number of trajectories led to the dissociation of an argon atom. To prevent overestimation of the DOS we have applied the method of Wales,[19] which adds a modified Lennard-Jones type potential to reflect the trajectory back to the region of strong interaction. This potential is

$$V(r_i) = \left\{ \begin{array}{ll} 4\epsilon\left[\left(\frac{\sigma}{R-r_i}\right)^{12} - \left(\frac{\sigma}{R-r_i}\right)^{6}\right] + \epsilon, & R - r_i < 2^{1/6}\sigma \\ 0, & R - r_i \geq 2^{1/6}\sigma \end{array} \right\} \tag{11}$$

In this work, we have taken $\epsilon = 0.01$ eV, $\sigma = 6.4345 a_o$, and $R = 30a_o + \sigma$.
The above modification of the potential is compatible with the conservation of the total energy and angular momentum in the strong interaction region.

As is shown in the next section, the definition of a transition state to separate the phase space into region-$(a)$ (solvated) and region-$(b)$ (non-solvated) allows us to calculate densities of states and thermodynamical quantities for each of these two separate species of $Mg^+Ar_{12}$.

From the total density of states, the heat capacity can be calculated from its definition[20] :

$$C_v(T) = \frac{\partial U(T)}{\partial T}, \tag{12}$$

where $U(T)$ is the mean energy at temperature $T$, which is defined by :

$$U(T) = \int_0^\infty \frac{E\,\omega(E) e^{-\beta E} dE}{Z(\beta)}. \tag{13}$$

## C. Harmonic model

To calculate the isomerization constants between the two regions of the phase space, we have used a simple harmonic model based on the RRKM approach which has recently been introduced by Kunz and Berry.[21] From the exploration of the potential energy surface, $N_m$ (= 83) minima and $N_s$ (= 137) saddle points have been found. We note $k_{ij}^{t_{ij}}(E)$ the rate constant to go from minimum $i$ to minimum $j$ through the transition state $t_{ij}$ which connects the two minima. In the RRKM theory this microcanonical rate constant is written as :

$$k_{ij}^{t_{ij}}(E) = \frac{1}{h} \frac{N_{ij}^{t_{ij}}(E)}{\omega_i(E)}, \tag{14}$$

where $h$ is the Planck's constant, $\omega_i(E)$ is the density of vibrational states at energy $E$ in the stable configuration $i$, and $N_{ij}^{t_{ij}}(E)$ is the number of vibrational states at energy $E$ of the transition state $t_{ij}$ defined by the potential energy $V^{t_{ij}}$. We have :

$$N_{ij}^{t_{ij}}(E) \ = \ \int_{V^{t_{ij}}}^{E} \omega_{ij}^{t_{ij}}(\epsilon)\ d\epsilon, \tag{15}$$

where $\omega_{ij}^{t_{ij}}$ is the vibrational density of states of the transition state $t_{ij}$.
In the harmonic approximation, the density of vibrational states in a stable configuration $i$ can be written as :

$$\omega_i(E) = \frac{E^{3n_a-7}}{(3n_a-7)!\ \prod_{k=1}^{3n_a-6} h\nu_i^k}, \tag{16}$$

where $\nu_i^1$, $\nu_i^2$, ..., $\nu_i^{3n_a-6}$ are the $(3n_a - 6)$ positive frequencies of the Hessian matrix in the minimum $i$ ($n_a$ here denotes the total number of atoms).

For the transition state, we obtain for the total number of vibrational states :

$$N_{ij}^{t_{ij}}(E) = \int_{V^{t_{ij}}}^{E} \frac{\epsilon^{3n_a-8}}{(3n_a-8)!\ \prod_{k=1}^{3n_a-7} h\nu_{ij}^k}\, d\epsilon, \tag{17}$$

where $\nu_{ij}^1$, $\nu_{ij}^2$, ..., $\nu_{ij}^{3n_a-7}$ are the $(3n_a - 7)$ positive frequencies of the Hessian matrix for the saddle point $t_{ij}$.

For large enough systems statistical independence of different pathways connecting two given wells can be assumed. We then obtain the rate constant for a transition from well $i$ to well $j$ as :

$$W_{ij}(E) = \sum_t k_{ij}^{t_{ij}}(E). \tag{18}$$

From the matrix $\mathbf{W}$ we can construct the linear Master equations for the time evolution of the probability distributions $\mathbf{P}(t) = [P_1(t), P_2(t), \ldots, P_{N_m}(t)]^+$, in which $P_j(t)$ is the probability for the system to be in the minimum energy configuration $j$ at time $t$. $+$ denotes a column vector. The evolution equations are

$$\frac{d}{dt}P_i(t;E) \;=\; \sum_{j=1}^{N_m} w_{ij}(E)P_j(t;E), \quad \text{for} \quad i = 1 \text{ to } N_m, \tag{19}$$

where we have let $w_{ij}(E) \;=\; W_{ij}(E) \;-\; \delta_{ij}\sum_{k\neq j} W_{kj}(E)$.

For different energies $E$, this linear system of equations can be solved analytically. Consequently, we can obtain the populations in all the minima as a function of time.

The populations at equilibrium condition ($t = \infty$) are given by

$$P_i^{eq}(E) = \frac{\omega_i(E)}{\sum_j \omega_j(E)}. \tag{20}$$

Hence, we compute the internal energy of the system from the equation

$$U(E) = E - \sum_i P_i^{eq}(E)V_i^0, \tag{21}$$

where $V_i^0$ is the potential at the bottom of minimum $i$. The above equation is used to construct the caloric curve at the harmonic approximation. The relation of $U(E)$ with temperature is given by the equipartition law

$$U(E) = (3n_a - 6)kT. \tag{22}$$

## D. Isomerization rate constants

To determine isomerization rate constants between two regions in phase space, (a) and (b), we define the populations $N_a(t)$ and $N_b(t)$ in these regions, respectively. $N_a(t)$ (resp. $N_b(t)$) is the sum of the populations in all the separate minima $i$ found in region $a$ (resp. $b$) at time $t$.

The equilibrium constant $K_{eq}$ between these two "isomer" populations can be written as :

$$K_{eq} = \frac{k_{b\to a}}{k_{a\to b}} = \frac{N_a(t=\infty)}{N_b(t=\infty)}. \tag{23}$$

$k_{a\to b}$ and $k_{b\to a}$ are the rate constants for the isomerization reaction (Eq. (2)).

The time evolution of these populations is given by :

$$\frac{dN_a}{dt} = -k_{a\to b}N_a + k_{b\to a}N_b. \tag{24}$$

From Eqs (23), (24) and the conservation relation :

$$N = N_a + N_b, \tag{25}$$

we obtain :

$$\frac{dN_a}{dt} = -(k_{a\to b} + K_{eq}\, k_{a\to b})N_a + K_{eq}\, k_{a\to b}N. \tag{26}$$

By defining :

$$k = (1 + K_{eq})k_{a\to b} \quad \text{and} \quad k' = K_{eq}k_{a\to b}, \tag{27}$$

we have

$$\frac{dN_a}{dt} = -kN_a + k'N. \tag{28}$$

The solution of this differential equation is

$$N_a(t) = \left[N_a(t=0) - \frac{K_{eq}N}{1 + K_{eq}}\right] e^{-kt} + \frac{K_{eq}N}{1 + K_{eq}}. \tag{29}$$

$K_{eq}$ is calculated from the ratio of harmonic DOS in regions $(a)$ and $(b)$. Thus, by fitting $N_a(t)$ to the results obtained from the solution of Master equations we can derive $k_{a\to b}$.

Equilibrium constants computed from the exact densities of states (Section B) are compared with the predictions of the harmonic model. However, the slowness of the isomerization process found in the numerical simulations does not allow a similar comparison for the rate constants. Hence, the multiple minima harmonic model is only used to estimate the isomerization rate constants.

# IV. Results

## A. Density of states and thermodynamic properties

We have first compared the DOS, as evaluated with the two different ensembles, canonical and microcanonical. As it was the case for Calvo and Labastie,[10] the results obtained for $Mg^+Ar_{12}$ are also in very good agreement. In Fig. 3, is displayed the logarithm of the DOS multiplied by the energy step $\Delta E$, computed from trajectories which are initialized in the absolute minimum of $iso$ $(b)$ (solid line). We have found that calculations with the canonical ensemble are more efficient at high energies, where a better sampling of phase space is required. On the other hand, microcanonical calculations are easier to carry out.

Also shown in Fig. 3 are the harmonic DOS (dashed lines). The lower curve (short dashed line) was obtained by taking in account only the absolute minimum, $\omega^h_{min-b}$, whereas the upper curve (the long dashed line) was obtained with the inclusion of all located minima accessible at energy $E$, $\omega^h$. We can see that a significant deviation from the $\omega$'s computed with Molecular Dynamics techniques is observed from energies of about 3 kcal/mol above the minimum.

Having the $\omega$'s we can calculate thermodynamical functions for the cluster. In Fig. 4, we compare the caloric curves obtained from *i)* direct averaging of the kinetic energy during Molecular Dynamics (filled squares), *ii)* the DOS derived from the microcanonical dynamics (solid line), *iii)* the DOS derived from canonical Nosé simulations (equally dashed line), and *iv)* the harmonic DOS derived from the harmonic model by including all the minima (double dashed line). In the second half of the picture the heat capacity of the cluster obtained using equations (12) and (13) in the three methods is presented.

A phase transition is predicted at ca. 50 K from both anharmonic DOS, extracted from canonical and microcanonical simulations. The harmonic DOS predicts a phase transition at ca. 70 K, and we can see that the variation of the slope in the caloric curve is not as abrupt as in the anharmonic calculations. This results in a broad peak of the heat capacity curve. We can also see that the smooth caloric curves obtained from the density of states show an earlier increase of the initial slope than the Molecular Dynamics averaging results. Of course, the large fluctuations of the Molecular Dynamics averaging in that region do not allow for an accurate evaluation of the phase transition temperature. The smooth aspect of anharmonic curves is a characteristic feature of the inversion procedure used in the multiple histogram method, which intrinsically averages out the fluctuations of fixed energy trajectories.

## B. Isomerizations

In order to test the assumption of the existence of a single transition state which effectively separates solvated and non-solvated structures, we have plotted in Fig. 5 the distributions of probability for the distance $R_{Mg^+-c.m.}$ (or simpler $R$) for several temperatures.

To derive them, we have stored the distributions $P_T(V,R)$ during constant temperature (Nosé dynamics) calculations, and averaged them over the values of the potential

$$P_T(R) = \int P_T(V,R)dV. \qquad (30)$$

We can see that at low temperatures $P_T(R)$ remains localized near the positions of the two symmetric isomers, since the trajectories initialized in the region of *iso* $(a)$ or *iso* $(b)$ can not escape to the other region. However, from 49.5 K and above, double-peaked distributions appear with a minimum at about 3.6 $a_o$. We also observe that, since the curves are normalized to unity, the area under region $(a)$ increases with the temperature to the expense of the area under regions $(b)$.

Figure 6 shows the average values of the potential as a function of $R_{Mg^+-c.m.}$ at two constant temperatures above 49.5 K :

$$\overline{V}(R) = \frac{\int V P_T(V,R)dV}{\int P_T(V,R)dV}. \qquad (31)$$

The two minima of the average potential function of the cluster separated by a single barrier is clearly seen in this figure. The minima are at the positions of the icosahedral structures, ($R_{Mg^+-c.m.} = 0$ for *iso* ($a$) and $R_{Mg^+-c.m.} = 5.5\ a_o$ for *iso* ($b$)). Notice also that the minimum of region ($a$) is much broader than that of region ($b$). The barrier occurs at ca. 3.6 $a_o$, although some temperature dependence is apparent. The potential on the large distances side increases with temperature. Based on the above results we have adopted a transition state for the isomerization between solvated and non-solvated conformers at $R_{Mg^+-c.m.} = 3.6\ a_o$

The phase transition seen in the caloric curve (Fig. 4) does not necessarily mean that a rapid isomerization between the solvated and non-solvated structures is taking place. This is testified in Fig. 7 where the average values of the distance of magnesium cation from the cluster center of mass, $< R_{Mg^+-c.m.} >$, obtained in the simulations are plotted versus total energy. In building this figure, some trajectories were initialized in the minimum of *iso* ($a$) (circles) and some in the minimum of *iso* ($b$) (squares). The root mean square fluctuation of the average Ar-Ar bond lengths is also shown. According to Lindemann's criterion a phase transition occurs when $\delta_{Ar-Ar}$ exceeds the value of 0.1. The two curves $< R_{Mg^+-c.m.} >$ and $\delta_{Ar-Ar}$ agree in predicting the temperature of the phase transition when the simulation is started from the *iso* ($a$) region in spite of the large fluctuations in $< R_{Mg^+-c.m.} >$. However, the results obtained with trajectories started in the minimum of *iso* ($b$) reveal a tendency of the aggregate to remain in region ($b$). This is in accord with the conclusions drawn from the *stationary point diagram* (Fig. 2).

In the integration time of 15 ns we observe an isomerization from region ($a$) to region ($b$) for first time at the energy of -19.2 kcal/mol. No other isomerization is recorded up to 18.7 kcal/mol, and only when the energy exceeds the phase transition point (50 K) we can see isomerizations again although not many.

Above the phase transition, the average values of $R_{Mg^+-c.m.}$ show that the system spends more time in region ($a$), i.e., the distance $< R_{Mg^+-c.m.} >$ is less than 3.6 $a_o$ for energies up to $-15$ kcal/mol, irrespectively of the fact that the trajectories are initialized in region ($b$). That indicates that the DOS of region ($a$) has become larger than the DOS of region ($b$) for these energies.

From these simulations it became apparent that isomerization events are rare even at high excitation energies. This result prevented us from estimating accurate rate constants by Molecular Dynamics calculations. However, we can accurately compute the DOS of each separate region in order to evaluate the equilibrium constants at several energies.

Fig. 8 displays the DOS of each separate region, ($\omega_a$) and ($\omega_b$). In the same plot the results given by the harmonic multiple minima model, ($\omega_a^h$), and ($\omega_b^h$) are also drawn. A characteristic feature of these curves is the crossing of the two DOS, $\omega_a$ and $\omega_b$, predicted by both models, anharmonic and harmonic. The intersection point is at $-18.6$ kcal/mol for the anharmonic calculations, and at $-18.3$ kcal/mol for the harmonic model.

Table I contains the equilibrium constants at the two levels of approximation, harmonic and anharmonic, the average harmonic rate constant ($K_{iso}^h$),

$$K_{iso}^h = \frac{1}{2}(k_{a\rightarrow b} + k_{b\rightarrow a}), \tag{32}$$

and average lifetimes in each region at the harmonic approximation for various values of the total energy $E$. Fig. 9 is a plot of $K_{iso}^h$ versus $E$. A substantial increase of the rate constant occurs at the energy of $-18.5$ kcal/mol, which coincides with the phase transition in the caloric curve and the intersection of the two DOS, $\omega_a$, and $\omega_b$.

## V. Discussion

In this work we have used the multiple histogram method to calculate vibrational DOS in both the microcanonical approach, recently proposed by Calvo and Labastie,[10] and the canonical approach. It is interesting that we found the two approaches to be equivalent, but the microcanonical method is quite appealing since the distributions of the potential values can be collected during an ordinary Molecular Dynamics simulation which is usually carried out at constant total energy. The canonical results were obtained by running "constant temperature" Nosé dynamics trajectories.[8,9] This requires the coupling of the system with a heat bath which is controlled with a coupling parameter $Q$. Obviously, the use and the test required to find a proper value for the coupling parameter $Q$ is a disadvantage of the Nosé method. We had some difficulties at very low temperatures in defining a proper value for this parameter. On the other hand, for a non-ergodic system like the $Mg^+Ar_{12}$ cluster, we have found that the fluctuations in the total energy which take place in constant temperature calculations assist the trajectory in sampling the phase space more efficiently. Therefore, we believe that both methods will be used in the future in a complementary fashion.

One of the aims of this project was to use approximate models, such as RRKM, to investigate complex isomerization reactions in rather large systems. Our assumption of a single effective transition state, and the calculation of the density and the total number of states analytically at the harmonic approximation, seem to be justified by the present findings. It is important to note that qualitative results which came out of the dynamical calculations, were predicted from what we call *stationary point diagram*. A careful search for finding extrema of the potential function of the cluster to reveal the morphology of the potential energy surface may be considered as the zeroth-order approximation to the dynamical behavior of the system. For systems with a small number of degrees of freedom a better exploration of the structure of phase space requires the location of other dynamical objects like periodic orbits and tori.[22]

Comparing Figs 2 and 6 we can see that the average potential follows the distribution of the stationary points along the reaction coordinate. The high density of the stationary points in the region of isomer ($b$) dictates that the trajectories will be trapped in this area of phase space for long times, at least for a particular range of energies. However, for energies higher than the energy of the crossing of the two DOS, the above situation is reversed. The latter is confirmed in Fig. 7 where trajectories remain in the region of isomer ($b$) for energies higher than in the case of region ($a$). It is our opinion, that the larger the system is and the better the search for stationary points is done, the more accurate the conclusions for the dynamics of the system, drawn from the *stationary point diagrams*, will be. Further research is required along this line.

Concerning the $Mg^+Ar_{12}$, the study of the isomerization reaction between the two symmetrical icosahedral conformers is an interesting problem, although, there is no experimental evidence about which type of the isomer is formed during its production.[3]

However, we believe that theoretical estimates of the equilibrium and rate constants will be useful for future experiments.

The assumption of an effective single transition state that separates the isomers has been proved to be valid for the present system. That allows us to calculate separately the DOS for each isomer, $\omega_a, \omega_b$, from trajectories which efficiently sample a smaller region of phase space. The DOS have been quite revealing. The intersection of the two curves at $-18.6$ kcal/mol implies that at higher energies isomer $(a)$ is favored with respect to isomer $(b)$. The intersection point almost coincides with the energy at which the phase transition from solid-like to liquid-like occurs. At the same energy the first isomerization events are recorded, although they are very rare.

Isomerization rate constants predicted with the harmonic model are of the order of $\mu s^{-1}$ at these energies, but rapidly increase to reach the order of $ns^{-1}$ at 2 kcal/mol above the crossing point. These values are in the same line with what we expect from the Molecular Dynamics calculations.

## VI. Conclusions

Isomerization processes among solvated and non-solvated conformers of $Mg^{+}Ar_{12}$ have been studied by computing densities of states, and from them, thermodynamical quantities and equilibrium constants. We have used canonical and microcanonical ensembles for the estimation of the densities of states and we found the two methods to be equivalent. The microcanonical method is free of the assumption of a heat bath and requires only the computation of distributions of the potential, something which is easy to get during customary Molecular Dynamics simulations.

Comparison of the equilibrium constants obtained from anharmonic and harmonic calculations show a satisfactory agreement for a substantial energy range. This is an encouraging output. It means, that the static information available from the *stationary point diagram* which portrays details of the morphology of the potential energy surface of the multidimensional system, can be extended into dynamical information with the harmonic approximation of DOS and the solution of Master equations for the evolution of the populations of each conformer. This is very important for studying the dynamics and kinetics of complex systems.

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## References


[1] W. H. Miller, Acc. Chem. Res. **26**, 174 (1993).

[2] D. G. Truhlar and B. C. Garrett, Annu. Rev. Phys. Chem. **35**, 159 (1984).

[3] M. Velegrakis and C. Luder, Chem. Phys. Letters **223**, 139 (1994).

[4] J. A. Northby, J. Chem. Phys. **87**, 6166 (1987).

[5] G. Fanourgakis and S. C. Farantos, J. Phys. Chem. **100**, 3900 (1996).

[6] J. S. Pilgrim, C. S. Yeh, K. R. Berry and M. A. Duncam, J. Chem. Phys. **100**, 7945 (1994).

[7] J. Papadakis, G. S. Fanourgakis, S. C. Farantos and M. Founargiotakis, J. Comput. Chem. **in press** (1996).

[8] S. Nosé, Mol. Phys. **52**, 255 (1984).

[9] S. Nosé, J. Chem. Phys. **81**, 511 (1984).

[10] F. Calvo and P. Labastie, Chem. Phys. Letters **247**, 395 (1995).

[11] W. Forst. *Theory of Unimolecular Reactions.* Academic, New York, (1973).

[12] H. Partridge, C. W. Bauschlicher Jr. and S. R. Langhoff, J. Phys. Chem. **96**, 5350 (1992).

[13] C. W. Bauschlicher Jr. and H. Partridge, Chem. Phys. Letters **239**, 241 (1995).

[14] W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling. *Numerical Recipes.* Cambridge Univ. Press, (1986).

[15] L. F. Shampine and M. K. Gordon. *Computer solutions of ordinary differential equations.* Freeman, San Francisco, (1975).

[16] P. Labastie and R. Whetten, Phys. Rev. Letters **65**, 1567 (1990).

[17] S. Weerasinghe and F. Amar, J. Chem. Phys. **98**, 4967 (1993).

[18] P. Parneix, F. Amar and P. Bréchignac, J. Chem. Phys. **104**, 983 (1996).

[19]D. Wales, Mol. Phys. **78**, 151 (1993).

[20]L. D. Landau and E. M. Lifshitz. *Statistical Mechanics.* Pergamon Press, New York, (1970).

[21]R. E. Kunz and R. S. Berry, J. Chem. Phys. **103**, 1904 (1995).

[22]S. C. Farantos, Int. Rev. Phys. Chem **15**, 345–374 (1996).

| E (Kcal/mol) | $K_{eq}$ | $K_{eq}^h$ | $K_{iso}^h$ ($\mu s^{-1}$) | $\tau_a^h$ ($ns$) | $\tau_b^h$ ($ns$) |
|---|---|---|---|---|---|
| -21.0 | 0.006 | 0.014 | | | |
| -20.5 | 0.023 | 0.052 | | | |
| -20.0 | 0.062 | 0.131 | | | |
| -19.5 | 0.173 | 0.257 | | | |
| -19.4 | 0.217 | 0.289 | | | |
| -19.2 | 0.344 | 0.364 | | | |
| -19.0 | 0.529 | 0.458 | | | |
| -18.8 | 0.769 | 0.578 | | | |
| -18.6 | 1.040 | 0.736 | 5.61 | 150 | 205 |
| -18.4 | 1.321 | 0.948 | 14.2 | 68.4 | 72.6 |
| -18.3 | 1.460 | 1.078 | 21.9 | 47.1 | 44.5 |
| -18.2 | 1.621 | 1.228 | 31.0 | 35.4 | 29.0 |
| -18.1 | 1.711 | 1.398 | 44.3 | 26.1 | 19.1 |
| -18.0 | 1.812 | 1.590 | 59.9 | 20.5 | 12.9 |
| -17.9 | 1.890 | 1.805 | 78.9 | 16.3 | 9.07 |
| -17.8 | 1.940 | 2.044 | 101 | 13.1 | 6.56 |
| -17.7 | 1.965 | 2.307 | 131 | 10.6 | 4.65 |
| -17.6 | 1.967 | 2.599 | 167 | 8.64 | 3.34 |
| -17.5 | 1.952 | 2.903 | 199 | 7.46 | 2.57 |
| -17.0 | 1.788 | 4.740 | 435 | 3.80 | 0.80 |
| -16.5 | 1.690 | 6.891 | 742 | 2.35 | 0.34 |
| -16.0 | 1.666 | 9.037 | 1085 | 1.66 | 0.18 |

TABLE I Equilibrium constants computed from the densities of vibrational states for the solvated and non-solvated isomers defined with the effective transition state, and using anharmonic ($K_{eq}$) and harmonic ($K_{eq}^h$) potentials. $K_{iso}^h$ is the average isomerization rate constant (Eq. (32)), and $\tau_a^h$ and $\tau_b^h$ are the average lifetimes of solvated and non-solvated $Mg^+$.

# Figure Legends

1. The two most stable isomers of $Mg^+Ar_{12}$ with icosahedral geometries. The energies are for $iso$ $(b)$ -23.589 kcal/mol and for $iso$ $(a)$ -23.056 kcal/mol.

2. The energies of the minima (filled squares) and transition states (open circles) found for the cluster $Mg^+Ar_{12}$, and arranged along the distance of magnesium cation from the center of mass of the cluster, $R_{Mg^+-c.m.}$; $R_{Mg^+-c.m.} = 0 \;\; a_o$ for $iso$ $(a)$ and $R_{Mg^+-c.m.} = 5.41 \;\; a_o$ for $iso$ $(b)$.

3. The logarithm of the density of vibrational states multiplied with the energy increment $\Delta E$. The solid curve was computed with the method of microcanonical ensemble, $(\omega)$. The long dashed line was computed using analytic harmonic formulae and all located minima up to energy $E$, $(\omega^h)$. The short dashed line is the number of states computed at the harmonic approximation but employing only the absolute minimum $iso$ $(b)$, $(\omega^h_{min-b})$.

4. (a) Caloric curves calculated with the microcanonical ensemble method (solid), canonical ensemble method (dashed), Molecular Dynamics averaging method (filled squares), and with the harmonic approximation (double dash line). Energies in kcal/mol. (b) Specific heats at constant volume computed from the caloric curves (see text). Units in kcal/(mol K).

5. Normalized distributions of the distance of $Mg^+$ from the center of mass of the cluster, $R_{Mg^+-c.m.}$, using constant temperature trajectories (see text).

6. The average value of the potential as a function of the distance of $Mg^+$ from the center of mass of the cluster, $R_{Mg^+-c.m.}$. The perpendicular bars show typical fluctuations of the potential.

7. (a) The average value of the distance of $Mg^+$ from the center of mass of the cluster, $< R_{Mg^+-c.m.} >$, and (b) the Ar-Ar bond length root mean square fluctuations at several energies. The squares denote the results obtained from trajectories initialized in the region of $iso$ $(b)$ and the circles trajectories initialized in the region of $iso$ $(a)$.

8. The logarithm of DOS multiplied with the energy increment $\Delta E$. $\omega_a$ and $\omega_b$ are the DOS calculated with the microcanonical method for the two separate regions of phase space $(a)$ and $(b)$. $\omega_a^h$ and $\omega_b^h$ are the DOS calculated at the harmonic approximation and using all located minima (see text). The insert shows the intersection of the two DOS.

9. The average isomerization rate constant (Eq. (32)).