Kinetics and equilibrium of small metallic clusters: Ab initio confinement molecular dynamics study of Au₄

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Abstract. The *ab initio* molecular dynamics (AIMD) [1] is combined with the heuristic, successive confinement method of surveying a potential energy surface (PES) [2], thereby offering a framework for the simulation study of kinetics and equilibrium properties of metallic clusters. This approach is applied to the study of Au₄, a cluster possessing a simple but specific PES, which consists of very shallow and deep basins and due to this presents a challenge to the conventional AIMD methods. Among other things, the probabilities of the transitions between isomers have been found, and on this basis, both the time-dependent and equilibrium populations of the isomers have been calculated for the conditions typical of the NeNePo experiments [3] in the femtosecond pump-probe spectroscopy.

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1 Introduction

The understanding of the mechanisms of isomerization processes in metallic clusters is of great importance both for the fundamental science and for numerous applications of the clusters in physics, chemistry and biology. For this, joint efforts from theory, experiment and computer simulations are required.

One rapidly developing field of experimental studies, which offers a close connection with simulations, is the femtosecond pump-probe spectroscopy of small clusters, in particular, the NeNePo technique [3]. It involves the preparation of an initial ensembles of the clusters in the anionic ground state, one-photon detachment by the pump pulse, the propagation of the system on the neutral electronic state, and the detection *via* the cationic ground state by a time-delayed ionizing probe pulse. The AIMD simulation study of the NeNePo process for a set of small metallic clusters has been performed in [1].

The goal of this paper is to work out a more general framework for the simulation study of metallic clusters. One approach, which has become conventional in molecular dynamics (MD) studies, is due to Stillinger and Weber (SW) [4], who suggested to quench the system at regular intervals in order to map the MD trajectory on the potential energy surface (PES). The approach is of a multipurpose character, allowing one to sample the PES of a system and to determine its equilibrium properties and

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kinetics. However, because of following the inherent dynamics of the system, computationally this approach is not as efficient as desirable. An example of this is given by Au₄, whose PES consists of very shallow and deep basins, and thus makes a homogeneous sampling of the PES very problematic.

A more efficient, heuristic approach, based on the confinement MD [5,6], was proposed recently [2]. It involves a guided sampling of a PES, and at the same time retains a multipurpose character of the SW approach. Here we implement this approach in the terms of the *ab initio* molecular dynamics (AIMD) [1] and apply it to the study of kinetics and equilibrium properties of Au₄.

2 The problem

The Au₄ cluster exists in the form of 3 isomers, which are rhombic, T-shape and linear structures [1] (labeled below as 1, 2 and 3); their characteristics are given in Table 1. The transition states (TSs) presented in Table 2 connect linear and T-shape isomers and T-shape and rhombic isomers, respectively. A schematic picture of the PES, based on these data, is shown in Figure 1.

Without restricting generality of the approach to be considered, let us turn to the conditions typical of the NeNePo experiments. First, the system is supposed to be in vacuum, and thus its total energy is conserved. The detachment by the pump pulse [1] at low temperature occurs for the linear isomer (or related zig-zag structure)
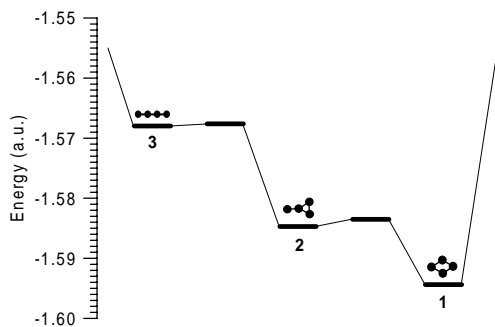
Table 1. Characteristics of the isomers: energies, U^0(a.u.), harmonic frequencies, ν^0(cm^{-1}), and vibrational periods (ps).

Isomer	1($\mathbf{D}_{2h}$)	2($\mathbf{C}_{2v}$)	3($\mathbf{D}_{\infty h}$)
U^0	−1.594328	−1.584677	−1.567974
ν_1^0	29.6(1.128)	9.5(3.502)	8.6(3.602)^a
ν_2^0	70.0(0.476)	27.2(1.225)	19.0(1.751)^a
ν_3^0	79.8(0.418)	71.9(0.463)	65.3(0.510)
ν_4^0	102.8(0.324)	73.9(0.451)	171.8(0.194)
ν_5^0	149.9(0.222)	171.0(0.195)	179.0(0.186)
ν_6^0	171.3(0.195)	184.4(0.181)	

^{a} Degenerate bending mode.

Table 2. Characteristics of the transition states: energies, U^*(a.u.), and harmonic frequencies ν^*(cm^{-1}).

TS	1 ↔ 2($\mathbf{C}_1$)	2 ↔ 3($\mathbf{C}_1$)
U^*	−1.583489	−1.567629
ν_1^*	20.1555	7.5694
ν_2^*	60.8404	13.6411
ν_3^*	102.1918	79.8640
ν_4^*	167.7477	160.5021
ν_5^*	177.3821	174.1527

Fig. 1. Schematic picture of the potential energy surface of Au$_4$.

which is the most stable anionic structure. Therefore, we conducted the simulations introducing the internal energy of the linear isomer corresponding to the temperature of about 100 K which is comparable to the TS barrier from linear isomer to T-shape isomer (108.6 K in temperature units). Under these conditions, we can expect that the system lives in the basin for linear isomer very short time, and when leaving this basin once, hardly returns to it.

In this situation, a straightforward way to obtain statistically representative data on the behaviour of the system would be to run a set of the MD trajectories started in the linear isomer basin at various atomic distortions and velocities taken from a thermal ensemble. However, since the TS barrier is very low, the thermalization of the system in this basin is difficult to achieve in a conventional way, i.e. by allowing the system to live in the basin for a sufficient time before leaving it.

An alternative approach, which not only solves this particular problem but is applicable to a variety of other problems, is a heuristic, successive confinement approach proposed in [2]. It offers essentially unlimited flexibility in the distribution of the residence times of a system in different regions of the PES, and thus a possibility to sample these regions as carefully as desirable.

3 Approach and computational background

The essential idea behind the approach is to confine the MD trajectory of the system successively to various basins on the PES, with the choice of basins for detailed examination and the length of time to be spent in the basins [2]. To control the basin that is currently sampled, the MD trajectory is mapped on the PES by regular identification of the atomic structures (at time intervals τ_q). For implementation of this approach, we need a method to generate phase trajectory of the system, a routine to identify a structure, and a procedure to confine the MD trajectory to a basin.

Ab initio molecular dynamics. To generate a phase trajectory of the system, we employed *ab initio* MD "on the fly" (i.e. without precalculation of the PES) based on the gradient corrected density functional approach with Gaussian atomic basis [7]. We use 1-electron relativistic effective core potential (1e-RECP) [8] with the parametrization given in reference [1]. The energy gradients were calculated analytically. Classical (Newtonian) equations of motion for nuclei were solved using the Verlet algorithm, with the time step of numerical integration equal to 1 fs.

Identification of structures. In order to determine to which isomer a current atomic structure should be related, we employed a combination of the quenching of the system with bondlength analysis. For the former, a standard steepest descent method was used, and for the latter we consider a bond length matrix $\mathbf{B} = \{b_{ij}\}$, where b_{ij} is the length of the bond between ith and jth atoms. Beforehand, each isomer (Tab. 1) was characterized by its potential energy $U^{0,l}$ and bond length matrix $\mathbf{B}^{0,l} = \{b_{ij}^{0,l}\}$, where l (=1, 2, 3) labels the isomers. With this, the procedure of identification of a current structure included a repeated set of three operations: (1) quenching the system, (2) calculating the bond length matrix of the quenched system, and (3) comparing this matrix with $\mathbf{B}^{0,l}$ ($l = 1, 2, 3$) by calculating the distance in bond space $\sum_{ij} | b_{ij} - b_{ij}^{0,l} |$. All possible permutations of the atoms for each isomer, dependent on the symmetry of the structure, were taken into consideration. The initial quench was taken to be deep, until the norm of the gradients was as low as 3×10^{-9} (all values, here and below, are in atomic units), and the subsequent quenches were restricted to 5 successful steps, i.e. the steps leading to a decrease of the energy. The structure was considered to be in the basin for a certain isomer if two successive sets of the operations satisfied the conditions: the potential energy of the structure at the output of the later set was lower than that for the preceding one, and this structure was closer in the bond space to an isomer, to which it was closest in the preceding set. This approach allowed us to

reduce the total number of evaluations of potential energy and gradients, which were required to identify a structure, approximately to one hundred, in average.

Confinement of the MD trajectory. When the system is supposed to be confined to a certain basin but is found outside this basin, it has to be returned into the basin. One way to do this, that was used in this work, is to place the system (*i.e.* its representative point) at the point where the system was found in the given basin last time, but instead of the atomic velocities that the system had at this point to use random values obeying a Maxwell distribution. Specifically, this procedure includes the following steps [6]: velocities are randomly chosen from a normalized Gaussian distribution, then overall translation and rotation of the cluster are excluded, and finally, the velocities are rescaled so that the kinetic energy of the cluster would be the same as it was at the point to which the system is returned.

4 Kinetics

Conventionally, kinetics is described using a master equation. However, another way is also possible, which is best suited to the confinement simulations [2]. Confining the system to a current basin (i), we can calculate the probability, q_{ji}, that the system will be found in basin j (including the original one, i) at the subsequent checking after a time interval τ_{q}. These quantities constitute the transition probability matrix $\mathbf{Q}(\tau_{\mathrm{q}}) = \{q_{ij}(\tau_{\mathrm{q}})\}$, which is related to the rate constant matrix, $\mathbf{W} = \{w_{ij}\}$, as

$$\mathbf{Q}(\tau_{\mathrm{q}}) = \exp(\mathbf{W}\tau_{\mathrm{q}}). \tag{1}$$

Having $\mathbf{Q}(\tau_{\mathrm{q}})$, and treating the transitions between isomers as a Markov process in the discrete time domain of checking intervals τ_{q}, we can calculate how the populations of the isomers $\mathbf{P} = \{p_i\}$ ($\sum_i p_i = 1$) change with time. They obey the equation

$$\mathbf{P}(t = k\tau_{\mathrm{q}}) = \mathbf{Q}^k(\tau_{\mathrm{q}})\mathbf{P}(t = 0) \tag{2}$$

where $\mathbf{P}(t = 0)$ is the vector of initial populations. Each multiplier in the product $\mathbf{Q}^k$ moves the system on time step τ_{q}. The equilibrium populations, $\mathbf{P}^{\mathrm{eq}}$, are obtained at $t \to \infty$, or can be found from the equation $\mathbf{P}^{\mathrm{eq}} = \mathbf{Q}\mathbf{P}^{\mathrm{eq}}$.

The diagonal elements of the transition probability matrix, q_{ii}, characterize lifetimes of the isomers. Assuming a Poisson distribution of the lifetimes, for the mean lifetime of the system in basin i we have

$$\tau_{\mathrm{life},i} = -\tau_{\mathrm{q}}/\ln q_{ii}. \tag{3}$$

A current lifetime can also be estimated directly, calculating the period of time (the number of checking intervals of the known length τ_{q}) during which the system did not leave the basin. Correspondingly, a manifold of the lifetimes for a given basin makes possible to build the lifetime distributions for this basin.

Table 3. Transition probabilities, q_{ij}, for the time interval of 0.1 ps. In brackets, there are given the corresponding values of q_{ij} obtained in the direct simulations.

Isomer from/to	1	2	3
1	0.937(0.932)	0.058(0.059)	0.0(-)
2	0.063(0.068)	0.942(0.941)	0.151(-)
3	0.0(0.0)	0.0(0.0)	0.849(-)

Table 4. Transition probabilities, q_{ij}, for the time interval of 0.1 ps, predicted by the RRKM theory *via* equation (1). The RRKM rate constants w_{ij} were calculated in the harmonic approximation, using the data of Tables 1 and 2.

Isomer from/to	1	2	3
1	0.875	0.501×10^{-1}	-
2	0.125	0.949	0.119×10^{-2}
3	-	0.469×10^{-5}	0.998

5 Results and brief discussion

The MD trajectory was successively confined to basins for linear, T-shape and rhombic isomers, until it made at least 100 attempts to leave the current basin. The cluster did not execute the overall translation and rotation, and its total energy, E, was equal to –1.566067 a.u., which corresponds to the heating of the linear isomer approximately to 110 K. The checking interval τ_{q} was equal to 0.1 ps.

Note, that in general case, when the variety of isomers is unknown, first one should find and characterize the isomers. This can be done by surveying the PES with the help of the successive confinement method [2,6,9].

In the course of the simulation, there were observed transitions from linear isomer to T-shape one, and also between T-shape and rhombic isomers. No transition from T-shape and rhombic isomers to the linear isomer has been detected. The corresponding transition probabilities are presented in Table 3. For comparison, Table 4 shows the values of q_{ij} that are predicted by the Rice-Ramsperger-Kassel-Markus (RRKM) theory [10]. It is seen that if the barrier is not so small as that for the linear-to-T-shape transition, the RRKM theory is reasonably accurate. We can thus suppose that the prediction for the probability of the transition from the T-shape isomer to the linear one is also correct, at least by the order of magnitude. Correspondingly, the time required to observe this transition in the simulations is 10^4 times larger than it is taken, in average, for a single act of the transition from the T-shape isomer to the rhombic one.

Figure 2 shows lifetime distributions for the isomers and their comparison with the theoretical (Poisson) distributions based on the mean lifetimes τ_{life} of Table 5. As seen, the lifetimes follow the Poisson law and are consistent with the values of mean lifetimes obtained from the transition probabilities.

Having the transition probabilities, we can use equation (2) to calculate time-dependent populations of the isomers for initial conditions of interest. Figure 3 shows
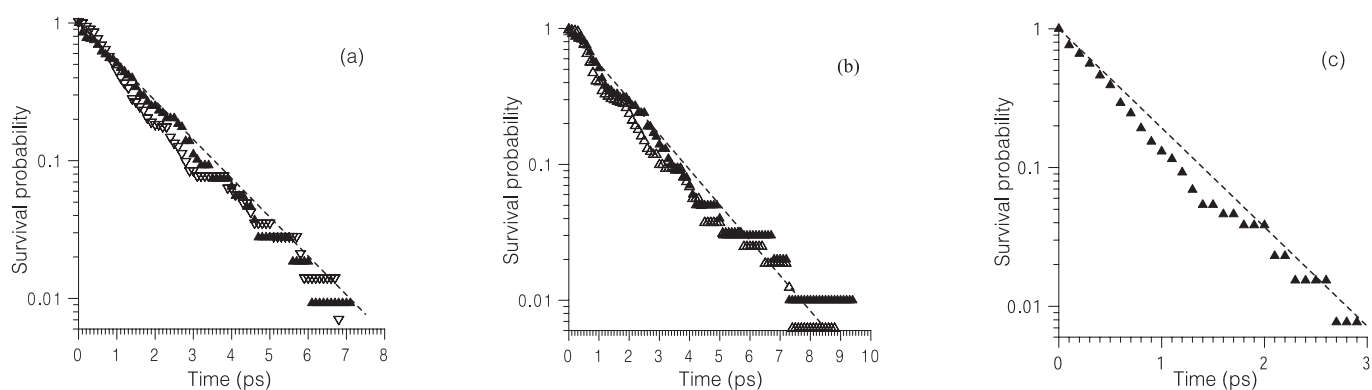
Fig. 2. Lifetime distributions for (a) rhombic, (b) T-shape, and (c) linear isomers. Solid and empty triangles label the confinement and direct simulations, respectively. Dashed lines show the Poisson distributions based on the mean lifetimes of Table 5.

Table 5. Mean lifetimes, calculated from the transition probabilities of Table 3 *via* equation (3), "temperatures" of the isomers, calculated from the kinetic energies of the system in the corresponding basins, and the equilibrium populations of the isomers from Figure 3. In brackets there are given the corresponding values found in the direct simulations.

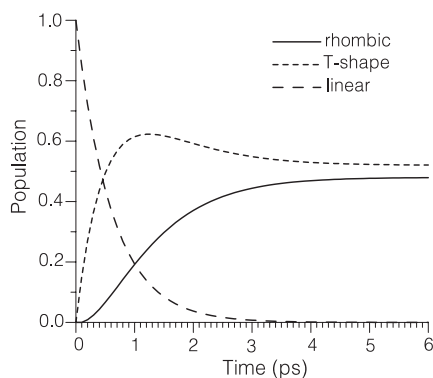| Isomer	τ_{life}, ps	T, K	p^{eq}
1	1.540(1.532)	1221(1225)	0.480(0.464)
2	1.672(1.721)	814(901)	0.520(0.536)
3	0.608(-)	110(-)	0.0(-)

Fig. 3. Time-dependent populations of the isomers.

such populations for a scenario characteristic of the NeNePo experiments. It is remarkable that though T-shape isomer is higher in energy than the rhombic one, which present the ground state atomic configuration of the cluster, its equilibrium population is higher. A reason is that the T-shape isomer, looser in constitution, samples larger conformation space than the compact rhombic isomer, and thus should have a larger conformation entropy.

Along with the confinement simulations we also performed a direct simulation, allowing the system to pass between the basins freely. The total energy of the system was as before, and the system started the exploration of

the PES in the basin for linear isomer. The total length of the run was 0.5 ns (5×10^5 time steps). The system left the basin for linear isomer in a short time (0.3 ps), and then kept making the transitions between T-shape and rhombic isomers (in total, approximately 150 transitions was made in each direction). In accord with the previously discussed RRKM estimates, the system never returned in the linear isomer basin for the given length of time. The results of the direct simulation are presented in Tables 3 and 5, and Figure 2, and they are in good correspondence with the confinement simulation results.

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