Ab initio molecular dynamics study on Agₙ (n = 4, 5, 6)

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Abstract. Ab initio Molecular Dynamics (MD) method, based on density functional theory (DFT) with planewaves and pseudopotentials, was used to study the stability and internal motion in silver cluster Agₙ, with n = 4−6. Calculations on the neutral, cationic and anionic silver dimer Ag₂ show that the bond distance and vibrational frequency calculated by DFT are of good quality. Simulations of Ag₄, Ag₅, and Ag₆ in canonical ensemble reveal distinct characteristics and isomerization paths for each cluster. At a temperature of 800 K, an Ag₄ has no definite structure due to internal motion, while for Ag₅ and Ag₆, the clusters maintain the planar structure, with atomic rearrangement observed for Ag₅ but not for Ag₆. At a temperature of 200 K, Ag₄ can exist in two planar structures whilst Ag₅ is found to be stable only in the planar form. In contrast Ag₆ is stable in both planar trigonal and 3D pentagonal structures. Microcanonical MD simulation was performed for all three clusters to obtain the vibrational density of states (DOS).

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1 Introduction

The electronic structure of small metal clusters has long been a subject of intensive theoretical and experimental studies, because of its importance for the understanding of metal-metal interactions, and in catalysis and photophysics [1–3]. Understanding the geometrical structure of these clusters is more challenging, since for each cluster there are often several possible isomers connected by a flat potential surface and thus the clusters do not have fixed structures due to isomerization and pseudorotation. The dynamics of such processes in small metal clusters as a function of temperature, first studied by classical molecular dynamics (MD) method, revealed interesting solid-liquid and liquid-gas-like transformations [4, 5], although designing an accurate empirical potential surface for these clusters is non-trivial. Recent development of ab initio molecular dynamics [6–12] offered a powerful new method to study such structural transformation, as the electronic energy and ionic force are calculated from first principle at either Hartree-Fock [13, 14], local density approximation [15, 16], or even post Hartree-Fock levels [17]. Alkali metal clusters, such as sodium [15, 16] and lithium clusters [13, 14, 17], have received most attention, since these systems are among the simplest with each metal atom contributing only one valence electron. The experimental progress in the high resolution spectroscopic measurement of metal clusters [18, 19], and especially the development of femtosecond laser system coupled with a negative ion-neutral-positive ion charge reversal apparatus which offers time resolved direct probe at the dynamics of the internal motion [20–22], are likely to provide further impetus for such theoretical efforts, especially for small clusters with n = 3–6.

Among transition metal clusters, silver clusters have received considerable attention from both experimentalists [18, 19, 21–29] and theoreticians [31–46]. In terms of electronic structure, transition metal clusters are more complicated than alkali metal clusters because of the presence of d electrons. However, a silver atom has a completely filled 4d-shell and one 5s valence electron, and silver clusters are often thought to be analogous to alkali metal clusters in terms of electronic configuration [33]. To date, the most detailed study on the Agₙ clusters used an effective core potential for the 4d shell and configuration interaction method to account for the correlation effects which were always important in transition metal species [31]. In addition, there is an extensive theoretical literature on the geometrical structures of Agₙ clusters at various accuracy levels [34–43]. Although these calculations may differ in their prediction of the most stable structure for some clusters (for example, Ag₅ and Ag₆ [31, 34, 40]), depending on the level of theoretical treatment and whether d electrons are included in the calculation, they agreed with each other in that each cluster

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of a certain size \((n = 3–9)\) was found to have several geometrical isomers which were close in energy, implying interesting vibrational dynamics for these clusters at constant temperature.

Classical molecular dynamics simulations have been performed very recently to study the dynamics of Ag$_6$, using a potential surface fitted to points in configuration space calculated by density functional theory [44–46]. The presence of \(d\) electrons has made \(ab\ initio\) MD simulations on silver clusters computationally much more demanding than simulations for alkali metal clusters. To our best knowledge no such studies have been reported in the literature except for Hartke and Carter’s \(ab\ initio\) MD study on Ni$_3$ cluster in which the \(d\) electrons were frozen [47].

In this article, we report an \(ab\ initio\) MD study on the dynamics of Ag$_n$, with \(n = 4–6\), taking advantage of the recent development of the spin-polarized non-local density method and of ultrasoft pseudopotentials [9–12]. After a careful study on neutral, cationic and anionic silver dimer to verify the quality of our method, we will explore the dynamics of the internal motion for Ag$_4$, Ag$_5$, and Ag$_6$, at temperatures ranging from 200 to 800 K, to see its dependence both on the cluster size and on temperature.

2 Computational method

The principles of \(ab\ initio\) MD method based on total energy calculation by density functional theory with a planewave basis set and pseudopotentials have been documented in the literature [6–8]. The \(ab\ initio\) total energy and molecular dynamics program VASP (Vienna \(ab\ initio\) simulation program) was used in the present study [9–12].

A silver cluster is put in a large cubic box to imitate gas phase conditions. The lattice parameter is 12 Å for silver tetramer, and 15 Å for dimer, pentamer and hexamer.

Ultrasoft pseudopotential for silver atom with the Ceperly-Alder type local exchange correlation functional [48], and with/without the Perdew-Wang [49] type generalized gradient correction (GGA), was used in the calculation. The silver potential was generated with a reference configuration of $d^{10}s^3$ and based on scalar relativistic wavefunctions with relativistic core-effects taken into account. Extensive tests on such potentials showed a significant reduction in the planewave cutoff energy [50], and for our simulation the cutoff energy was 180 eV. Unless specified otherwise, the spin-restricted method was used for closed shell clusters and the spin-unrestricted for open shell clusters. The optimization for total electronic energy was performed by conjugate gradient method, and cluster structures reported by Bonačić-Koutecký et al. [31] were used as the starting point for geometrical optimization.

To investigate the thermal stability of Ag$_n$, \(n = 4–6\), molecular dynamics (MD) calculations in the canonical ensemble with a Nosé-Hoover thermostat [51] were performed. Time step used in the MD simulations was 2 fs. Atomic Equivalence Index (AEI) as defined in reference [14] is a very sensitive order parameter to monitor structural changes and is used in the analysis of the trajectories. For the \(i\)th atom, AEI(\(\sigma\)) is given as,

$$\sigma_i = \sum_{j \neq i} |r_i - r_j|$$

and the summation is over all distances from atom \(i\) to all other atoms within the cluster. In addition, the root-mean-square bond length fluctuations, \(\delta\),

$$\delta = \frac{2}{n(n-1)} \sum_{i<j} \left( \frac{(r_{ij}^2) - \langle r_{ij} \rangle^2}{\langle r_{ij} \rangle} \right)^{1/2}$$

is also calculated to measure thermal stability and to be compared with previous MD simulations on Ag$_6$ [44].

Micro-canonical MD simulations were also performed on selected isomers for Ag$_4$, Ag$_5$, and Ag$_6$. The time step used was again 2 fs, and total duration was 10 ps (5000 steps). The atom velocity correlation function and its Fourier transform was then calculated. When the simulation duration is varied, peak positions change very little, while peak widths change slightly. The peak height so obtained is proportional to the density of states, rather than the experimental IR intensity.

3 Results and discussion

3.1 Ag$_2$

Ag$_2$ is the simplest and most studied silver cluster, therefore a good model to test the quality and accuracy of our computational procedure. We conducted a detailed study on the neutral silver dimer and its cation and anion. For each species, about 40 points on the potential surface were calculated with internuclear distance ranging from 1.8 to 4.0 Å. These points were numerically fitted to a Morse potential to extract the equilibrium bond distance and vibrational frequency. The dissociation energy was calculated from the energy difference between the dimer and the corresponding isolated atom/ion. Four different levels of approximation were used in the calculation: local density approximation (LDA), spin-polarized LDA (LSDA), Perdew-Wang gradient corrections (GGA) [49], and spin-polarized GGA. The results obtained here are compared with previous experimental and theoretical studies in Tables 1 and 2.

In general, the calculated bond distances and vibrational frequencies are in good agreement with previous experimental and theoretical results. The dissociation energy is often overestimated, but GGA and spin-polarization improve the results. GGA are used for all subsequent simulations. For closed-shell Ag$_4$ and Ag$_6$, spin-restricted calculation is performed. In the early days of the application of the \(ab\ initio\) molecular dynamics method to metal clusters, spin-restricted method was often employed even for open-shell systems. To examine the validity of this simplification, both spin-polarization and spin-restricted methods are attempted for the open-shell Ag$_5$ cluster.