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► **To cite this version:**

J. Jiang, Marius Lewerenz. Quantum Simulation of  $\text{Mg}^+\text{He}_n$  and  $\text{Ar}^+\text{He}_n$  Clusters. 17th Symposium on Atomic and Surface Physics and Related Topics (SASP 2010), Jan 2010, Obergurgl, Austria. pp.185-188. hal-00832556

**HAL Id: hal-00832556**

**<https://hal.science/hal-00832556>**

Submitted on 11 Jun 2013

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# Quantum Simulation of $\text{Mg}^+\text{He}_n$ and $\text{Ar}^+\text{He}_n$ Clusters

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We present accurate quantum Monte Carlo calculations of the stability and structure of  $\text{Mg}^+\text{He}_n$  and  $\text{Ar}^+\text{He}_n$  clusters using accurate many-body potential surfaces derived from high level ab initio calculations and including spin-orbit effects in the case of  $\text{Ar}^+$ . The highly quantum nature of the nuclear motion in these systems leads to significant delocalisation such that no sharp shell closure is found for  $\text{Mg}^+$  doped helium clusters whereas the interactions are sufficiently strong in  $\text{Ar}^+$  doped clusters to allow the appearance of magic numbers.

## Introduction

Neutral helium clusters are extreme quantum systems whose cohesive energy pattern is controlled by their immense zero point energy arising from the combination of a small mass with very weak van der Waals interactions [1]. The implantation of one or several atomic and molecular dopants D into these clusters originally developed to understand the structure of the helium cluster itself has developed into an almost routine technique for the spectroscopic observation of stable species and reactive intermediates [2,3] and otherwise hard to prepare molecular or metal cluster systems [4,5]. The final step of most experiments involves ionization of the neutral  $\text{D@He}_N$  system and leads to the formation of a series of smaller fragment ions of the type  $\text{D@He}_n$ ,  $n \ll N$ . The relative abundance of individual mixed cluster ions reflects a complicated superposition of the relative stability of product ions and the actual fragmentation dynamics. The assumption of an almost thermodynamical situation often appears justified such that a correlation can be established between theoretical predictions of relative stabilities and observed relative ion count rates. Complementary information on stability patterns comes from ion drift tube experiments where mixed cluster ions are formed in multiple collisions of a dopant ion with helium atoms [6].

Rare gas ions were among the first species to be observed as dopants in helium clusters [7]. Accurate theoretical modeling of  $(\text{NeHe}_n)^+$  [8] showed distinct, but complicated, binding hierarchies in agreement with experimental observations. Metal ions have attracted increasing interest in experiments aiming at the creation of reactive metal clusters like  $\text{Mg}_m$  and the search for extreme coordination numbers [9, 10]. The  $\text{Mg}^+$  ion has an isotropic interaction of moderate strength with helium atoms through a  $^2\Sigma^+$  state and is thus an ideal candidate for methodological tests and comparison with ionization experiments. Heavier rare gas ions like

$\text{Ar}^+$  present additional challenges for theoretical modelling due to the presence of a strongly attractive  $^2\Sigma^+$  state and a shallow  $^2\Pi$  state and spin-orbit splitting in the  $^2P$  atomic ground state which is comparable with the van der Waals well depths and therefore strongly influences the effective interaction potential.

## Computational details

The  $\text{Mg}^+ - \text{He } ^2\Sigma^+$  interaction potential of Gardner and Wright [11] which is based on CCSD(T) coupled cluster calculations with extrapolation to the complete basis set limit was fitted to an undamped HFD form with a leading  $C_4 r^{-4}$  term which accounts for the dominant long range charge-induced dipole interaction. For  $\text{Ar}^+ - \text{He}$  we carried out CCSD(T) calculations with the MOLPRO suite of programs [12] and the full sequence of cc-pVXZ and aug-cc-pVXZ, X=2-6, basis sets developed by Dunning and coworkers [13]. The ab initio data for both  $^2\Sigma^+$  and  $^2\Pi$  states were fitted to the same undamped HFD form as above.

The many body surface for  $\text{Mg}^+\text{He}_n$  for the diffusion quantum Monte Carlo (DMC) calculations was constructed as a sum over pairwise contributions with additional terms accounting for the interaction between the induced dipoles carried by the helium atoms and using the experimental polarisability value. For  $\text{Ar}^+\text{He}_n$  a full complex 6x6 spin-orbit matrix was constructed for each particle arrangement with diagonal elements given as sums over pairwise  $\Sigma$  and  $\Pi$  contributions using the appropriate projections with additional induction terms and off-diagonal elements computed from the experimental atomic  $^2P_{3/2}/^2P_{1/2}$  splitting of  $1431.6 \text{ cm}^{-1}$  [14]. The lowest eigenvalue of the matrix was used as potential energy input to propagate the random walkers within the DMC method.

Our DMC calculations were carried out with fixed ensembles of 1000 – 16000 weighted random walkers, imaginary time steps between 10 and  $100 E_h^{-1}$ , and Jastrow/Fermi type trial wave functions as described in our earlier publications [8]. In spite of the use of trial wave functions a significant ensemble size bias on energies was observed such that extrapolations to infinite ensemble size were necessary for  $n > 10$ .

## Results and discussion

Our CCSD(T) calculations for  $\text{Ar}^+\text{He}$  showed several unexpected features. Convergence of the shape and depth of the  $^2\Sigma^+$  and  $^2\Pi$  wells with respect to basis set size was very slow within the cc-pVXZ series such that even at sextuple zeta, X=6, level no satisfactory convergence was found. The inclusion of diffuse basis functions in the aug-cc-pVXZ series dramatically improves the convergence but still leaves an uncertainty margin of several  $\text{cm}^{-1}$  for the well

depths of about 435 and 142  $\text{cm}^{-1}$  for the  $\Sigma$  and  $\Pi$  states, respectively. The conventional counterpoise correction performs very badly in particular for the ground state. Our final interaction potentials were computed by extrapolation to infinite basis set size using separate exponential and inverse power dependencies for the Hartree-Fock and correlation parts, respectively [15]. The quality of our final potential curves was checked by numerical solution of the radial Schrödinger equation for the X,  $A_1$ , and  $A_2$  states arising from the spin-orbit treatment for  $\text{Ar}^+\text{He}$ . We obtained wave numbers of 92.5 and 64.9  $\text{cm}^{-1}$  for the  $v=0 \rightarrow v=1$  and  $v=1 \rightarrow v=2$  vibrational transitions in the X state which compare very well with the experimental values of 92.9 and 66.2  $\text{cm}^{-1}$  [16]. For the  $v=0 \rightarrow v=1$  transition observed in the  $A_2$  state we find 69.2  $\text{cm}^{-1}$  in perfect and probably somewhat fortuitous agreement with experiment [16].

The total energies from our DMC calculations for  $\text{Ar}^+\text{He}_n$  show a marked effect of spin-orbit coupling on the structure of small clusters. Neglect of this effect strongly favors the first two helium atoms which can approach  $\text{Ar}^+$  along the deep  $^2\Sigma^+$  potential from opposite sides. This preference is significantly reduced due to the mixing of  $\Sigma$  and  $\Pi$  character which reduces the overall anisotropy of the potential. The common magic number of  $n=12$  which is found in the sequence of minimum energy structures for our many body model becomes non magic upon inclusion of zero point energy when spin-orbit coupling is neglected. It reappears as magic in agreement with ion drift tube [6] and large neutral cluster ionization experiments [8] in our full treatment accounting for spin-orbit coupling and zero point energy.

For  $\text{Mg}^+\text{He}_n$  clusters our accurate DMC calculations contradict the pronounced shell structures obtained in the approximate variational Monte Carlo study of Rossi et al. [17]. We find a smooth build up of helium density in a first layer around  $\text{Mg}^+$  which reaches saturation at  $n=18$  or 19 at a density of 0.07  $\text{\AA}^{-3}$ , approximately three times the bulk liquid helium density. The energy pattern shows approximately constant binding energy increments near 50  $\text{cm}^{-1}$  up to  $n=10$  which thereafter slowly decrease to about 12  $\text{cm}^{-1}$ , a value reached at  $n=18$ . There is no sharp transition between binding energy regimes which would correspond to shell formation. In fact the radial density build up beyond  $n=19$  shows that the density minimum following the nearest neighbor maximum never drops below values of about 0.01  $\text{\AA}^{-3}$ , a situation which is incompatible with the interpretation as a solid 'snowball'.

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