

**Theoretical modeling of ionization energies of argon clusters –  
nuclear delocalization effects.**

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## Abstract

Temperature dependence of vertical ionization energies is modeled for small argon clusters ( $N \leq 13$ ) using classical parallel-tempering Monte Carlo methods and extended interaction models based on the *diatomics-in-molecules* approach. Quantum effects at the zero temperature are also discussed in terms of zero-point nuclear vibrations, either at the harmonic approximation level or at the fully anharmonic level using the diffusion Monte Carlo calculations. Both approaches lead to a considerable improvement of the theoretical predictions of argon clusters ionization energies and represent a realistic way of modeling of ionization energies for weakly bound and floppy complexes in general. A thorough comparison with a recent electron-impact experiment [O. Echt *et al.*, J. Chem. Phys. 123 (2005) 084313] is presented and a novel interpretation of the experimental data is proposed.

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## I. INTRODUCTION

Rare-gas clusters, both neutral and ionic, have long been model systems for the cluster science [1]. From the experimental point of view, the neutral clusters can easily be produced via nozzle expansion and subsequently ionized either by photons or electrons. The ionic clusters can then be easily size selected and further manipulated. For theoreticians, the rare-gas clusters are simple to treat, which holds even for the ionic clusters in which many electronic states are usually involved. Consequently, the rare-gas clusters have received a considerable attention in the past. Among others, ionization and following post-ionization fragmentation of size-selected rare-gas clusters, argon in particular, have been studied intensively in experiment [2–6] as well as in theory [5, 7–9]. Despite of this considerable effort, many questions concerning the ionization of rare-gas clusters still remain open. The following example is just one of them.

It is usually believed that photoionization should lead to threshold energies close to the adiabatic ionization potential because Rydberg autoionizing states of the neutral precursor are involved. Electron-impact ionization, on the other hand, is expected to occur at considerably higher energies for which the vertical ionization potential is the lower limit [5]. Recent experimental data on the ion appearance energies reported for argon [5] seem to contradict this widespread assumption as they lie well below the vertical ionization potentials of  $\text{Ar}_N$  for cluster sizes  $N \leq 10$ . Similar behavior was also observed for helium and interpreted in terms of the autoionizing states of neutral clusters generated in collisions with impacting electrons [10]. This is clearly illustrated in Fig. 1 (see Sec. II for computational details) where vertical ionization potentials calculated using several *diatomics-in-molecules* models for  $\text{Ar}_N^+$  (the upper family of step-wise curves) are compared with the experimental data of Ref. 5 (full dots). Note, however, that the theoretical data of Fig. 1 as well as those used in Fig. 4 of Ref. 5 have been calculated for frozen equilibrium geometries of neutral precursors,  $\text{Ar}_N$ , and possible distortions of classical structures, either due to quantum zero-point vibrations for  $T = 0$  K or thermal excitations at  $T > 0$  K, have not been taken into account. It is the main aim of this paper to analyze how much the neutral cluster distortions are important for the theoretical modeling of the ion appearance energy of argon clusters. We use quantum calculations, either at the harmonic approximation level or fully anharmonic based on the *diffusion Monte Carlo* approach [11, 12], to assess the role of quantum effects at the zero

temperature, and classical parallel-tempering Monte Carlo simulations [13, 14] to see the role of thermal excitations at non-zero temperatures. Based on the computational results, we show that geometry distortions of floppy argon clusters must be taken into account when interpreting experimental electron-impact ion appearance energies of Ref. 5. Since these distortions lead to delocalized positions of argon nuclei in the cluster configuration space, we denote the effects of these distortions as *nuclear delocalization effects*.

## II. METHODS AND COMPUTATIONS

At a semi-classical level, the vertical ionization potential (VIP) is calculated for a given geometry of  $\text{Ar}_N$  as

$$\Delta E = E_{\text{ion}} - E_{\text{neut}}, \quad (1)$$

where  $E_{\text{ion}}$  and  $E_{\text{neut}}$  are total electronic energies of  $\text{Ar}_N^+$  and  $\text{Ar}_N$ , respectively, pertinent to the particular cluster geometry. Note that if classical equilibrium geometry of the neutral is used in Eq. 1 for both the neutral and the ion, classical zero-temperature VIP is obtained. We will denote this quantity as  $\text{VIP}_e$  in this work. If the zero-point energy is included for the neutral cluster to represent quantum effects at  $T = 0$  K at the crudest level, an alternative acronym,  $\text{VIP}_0$ , will be used.

In experiments, many cluster geometries contribute to the recorded experimental signal. For non-zero temperatures, thermal excitations distort the cluster geometry, and even at temperatures close to zero quantum zero-point vibrations lead to non-negligible structure distortions. Different structure distortions may naturally lead to more or less different ionization energies, and, consequently, a gradual rise of the ionic signal is observed if the impact energy is increased. This signal increase can be represented via a simple function [15],

$$f(E) = \begin{cases} b & \text{for } E \leq E_0, \\ b + c(E - E_0)^p & \text{for } E > E_0, \end{cases} \quad (2)$$

where  $E_0$  represents the threshold energy at which ions of a given size emerge from experimental noise,  $b$ , and is thus called *ion appearance energy* (IAE).

In theoretical treatment, contributions from distorted geometries can be modeled by generating a representative set of neutral cluster configurations and summing up the number of configurations having the vertical ionization energy below a given value of the impact

energy,  $E$ . Similar curves are then obtained to those recorded in experiments (see, e.g., Fig. 2 and the discussion in Sec. III) and theoretical predictions of IAEs can be extracted from these curves by least-squares fitting of an appropriate analytical formula, e.g., that given in Eq. 2. In this work, we use, together with Eq. 2, an alternative functional form of  $f(E)$  to correlate simulated data which models the threshold part of the theoretical ionic signal a bit better than Eq. 2, namely, a truncated Taylor expansion of the energy dependence of the ionic signal in the right vicinity of  $E = E_0$ ,

$$f(E) = b + \sum_{k=1}^6 c_k (E - E_0)^k, \quad E > E_0. \quad (3)$$

The truncation on the r.h.s. of Eq. 3 has been set at  $k = 6$  because the fitted values of the exponent of Eq. 2 are always below 6. Naturally, the noise parameter,  $b$ , is set to zero in both fitting models for the noise-free theoretical data.

Three simulation strategies have been used for generating sets of  $\text{Ar}_N$  configurations in this work: a) canonical parallel-tempering Monte Carlo (c-MC) simulations [13, 14] yielding ionic signal profiles at non-zero cluster temperatures at the classical level, b) sampling from the square of harmonic zero-point vibration functions [16–18], constructed using Hessian matrices calculated at the equilibrium configurations of  $\text{Ar}_N$ , to assess the role of quantum effects at the harmonic approximation level (hereafter denoted as q-HA), and c) an importance sampling algorithm [12] for the diffusion Monte Carlo approach (denoted as q-DMC), using high-quality Boltzmann-like trial wave functions optimized for  $\text{Ar}_N$  [19], to assess the effect of the anharmonic shape of the  $\text{Ar}_N$  potential energy surfaces (PESs). Note that the importance sampling algorithm in the DMC approach generates configurations sampled from a distribution given by the product of the trial function and the true vibration ground-state function and, because of the closeness of the two functions, sampling from the square of the vibration ground-state function is effectively achieved. The total number of cluster configurations considered for each cluster size and for each temperature is 100,000 (with each two successive configurations generated in c-MC calculations interleaved with 50 whole cluster moves to avoid non-physical correlations).

The energies required in Eq. 1 have been calculated using the HFDID1 pairwise potential [20] and a three-body *ab initio* potential [21, 22] for neutral  $\text{Ar}_N$ , and employing recently developed models [9, 18, 23] based on the *diatomics-in-molecules* (DIM) approach [24, 25] for ionic  $\text{Ar}_N^+$ . For the neutrals, two interaction models have thus been used, either a purely

pairwise additive model (we denote it as N[2] in this work) or a model including both pairwise and three-body contributions, which we denote as N[23]. For the ionic species, four previously reported and tested models [9, 18] have been used, a model based on the original DIM methodology developed for rare-gas cluster cations [25] (denoted here as I[d]), a model incorporating the spin-orbit (SO) coupling in  $\text{Ar}^+$  [26] via the *atoms-in-molecules* approach [27] (I[ds]), another model extending the I[ds] model by considering the most important polarization three-body interactions of the induced dipole – induced dipole type [26] (I[dsi]), and the most comprehensive model including, in addition to other corrections, neutral dispersion forces [28] (I[dsin3]). By combining the two interaction models for the neutral clusters and the four models for the ionic species we could get a broad set of data allowing to assess particular roles various interaction contributions play in IAE calculations. In the present study we have used the following four combinations of models: N[2] & I[d] (hereafter denoted as N[2]I[d]), N[2] & I[ds] (denoted as N[2]I[ds]), N[2] & I[dsi] (denoted as N[2]I[dsi]), and N[23] & I[dsin3] (denoted as N[23]I[dsin3]), which enable us to estimate the importance of the SO coupling contribution and the contributions due to polarization and dispersion three-body forces.

Since the zero energy reference states used in the calculations described in the preceding paragraph are different for the neutral precursor and ionic daughter cluster ( $N$  neutral atoms for the neutral cluster while  $(N - 1)$  neutral atoms plus an ion for the ionic daughter), the energy difference between the reference states (here, the atomic ionization potential) must be added to the r.h.s. of Eq. 1. The value has been taken from experiment [5, 29] with the SO coupling contribution removed,  $\text{IP}(\text{Ar}) = 15.798 \text{ eV}$ . Removing the SO interaction from  $\Delta E(\text{Ar})$  is necessary as the zero of the ionic interaction energy has been set in our models to the energy of the fully atomized state of  $\text{Ar}_N^+$  calculated within the I[d] model, i.e., with the SO coupling excluded.

The accuracy of the DIM-based models used in this work has been checked against the vertical ionization potentials obtained for classical equilibrium geometries of  $\text{Ar}_2$  and  $\text{Ar}_3$  from non-relativistic, spin-free calculations at the CCSD(T)/d-aug-cc-pV5Z level of the theory [30]. The *ab initio*  $\text{VIP}_e$  differs only by  $-21 \text{ meV}$  from the value obtained from the N[2]I[d] model for  $\text{Ar}_2$  and by  $-47 \text{ meV}$  from the value calculated using the N[23]I[dsin3] model for  $\text{Ar}_3$ . This clearly demonstrates a high reliability of our semiempirical modeling.

### III. RESULTS AND DISCUSSIONS

Let us start our discussion with an overview of calculations performed for classical equilibrium geometries of argon clusters as optimized via a previously developed genetic algorithm method [31]. Results are displayed in Fig. 1. The vertical ionization potentials,  $VIP_0$  and  $VIP_e$ , have been calculated using Eq. 1 and equilibrium geometries of  $Ar_N$ , the adiabatic ionization potentials,  $AIP_0$ , have been obtained by using equilibrium geometries of the neutral clusters for  $E_{\text{neut}}$  and equilibrium geometries for the ionic daughters for  $E_{\text{ion}}$  (in both cases with the zero-point energy included). While only the N[2]I[dsi] model has been used for  $AIP_0$  and  $VIP_e$ , the  $VIP_0$  calculations have been performed for all the interaction models considered in this work. Data obtained for the most comprehensive model N[23]I[dsin3] are not shown in Fig. 1 as they almost coincide with the data obtained for the N[2]I[dsi] model, probably due to heavy cancellation of the dispersion three-body contributions in the neutral and ionic species. Consequently, we have performed most of our calculations presented in this work for the N[2]I[dsi] model. For comparison, results of recent electron-impact [5] and TPEPICO [4] experiments are also shown in Fig. 1. Other photoionization data [3] available in the literature for cluster sizes considered in this work are not included for brevity as they are close to the data of Ref. 4. One important conclusion can be drawn from Fig. 1 which complies well with the observation of Ref. 5, namely, that the electron-impact IAEs are well below the theoretical VIPs for the smallest cluster sizes (up to  $N \approx 10$ ), which contradicts a general assumption that electron-impact experiments should bound theoretical VIPs from above. Considering the theoretical data depicted in Fig. 1 by themselves, it is clear that the inclusion of the SO coupling does not change the VIP curve much (as demonstrated for  $VIP_0$ , cf. the N[2]I[d] and N[2]I[ds] curves), while the three-body polarization forces included in the N[2]I[dsi] model change  $VIP_0$  notably, in particular for larger cluster sizes. As already mentioned, no significant change occurs if the three-body dispersion forces are taken into account. Furthermore, the inclusion of the zero-point vibration energy has only minor effect in the smallest clusters and becomes important only for larger cluster sizes.

After having analyzed the results of VIP calculations performed for localized, classical equilibrium structures of  $Ar_N$ , let us proceed to the important question how the structural deformations of  $Ar_N$  change the picture. Illustrative examples of various theoretical modelings of the ionic signal originating from distorted (delocalized) argon cluster configurations

are given for a particular cluster size,  $N = 7$ , in Fig. 2. Clearly, the ionization energy calculated for the equilibrium geometry of  $\text{Ar}_7$  (and corrected for the zero-point energy,  $\text{VIP}_0$ ) is considerably above the experimental IAE, whereas the threshold ionization energies move notably towards experimental uncertainty limits if distorted cluster configurations are considered. For example, the two quantum calculations performed for  $T = 0\text{ K}$  lead to IAEs comparable with the experimental data (q-DMC) or even below them (q-HA). Alike, the data obtained for non-zero temperatures from classical MC calculations (c-MC) are also considerably pushed toward experimental values, though not as much as the data obtained from quantum calculations. This is also seen in Table I where fitted IAEs are summarized for all the profiles depicted in Fig. 2 and for both fitting strategies introduced in Eqs. 2 and 3.

The behavior of the theoretical ionic signal profiles of Fig. 2 can be easily understood if one realizes that the equilibrium structures of ionized clusters are shrunken with respect to the equilibrium structures of their neutral precursors and, consequently, configurations of  $\text{Ar}_N$  with contracted inter-atomic distances contribute mainly in the threshold region of the ionic signal. Such configurations rest mainly on the repulsive wall of the neutral cluster PES, but still lie in the attractive region of the PES of its ionic daughter (see a schematic sketch in Fig. 3). For the classical equilibrium geometry of the neutral parent, we are far on the asymptotic part of the ionic PES and, consequently, the calculated VIP is too high even if the zero-point energy of the neutral cluster is included ( $\text{VIP}_0$ ). Calculations comprising distorted  $\text{Ar}_N$  geometries lead, on the other hand, to a considerable decrease of the impact energy needed to ionize the neutral cluster. It is because the cluster is allowed to climb the repulsive wall of the neutral PES and geometries closer to the equilibrium structure of the ionic daughter are involved. For a given vibration excitation of the neutral cluster (e.g., by the zero-point energy), this can occur only within classical turning-point limits in classical simulations (c-MC), but these limits can be surpassed in the quantum treatment. Consequently, the quantum ionic signals are shifted to lower threshold ionization energies with respect to the classical curves, and this is even true if higher temperatures are considered in classical simulations (see Fig. 2). The harmonic approximation to the neutral PES is too shallow in the repulsive region and provides unrealistically favorable conditions for penetrating the repulsive parts of the neutral PES, which further shifts the threshold for  $\text{Ar}_N$  ionization to lower impact energies. It is thus not appropriate for the quantitative modeling of quantum effects on IAEs for floppy argon clusters. It should be emphasized here that the



differences seen between IAEs calculated within the harmonic approximation approach and those obtained from fully anharmonic calculations via the DMC method cannot be attributed to the differences between harmonic and anharmonic zero-point energies (see Table II) and are clearly due to the insufficiency of the harmonic approximation in the classically forbidden regions.

As is clear from the previous discussion on  $\text{Ar}_7$ , the inclusion of delocalized structures of neutral clusters can decrease the threshold ionization energies considerably and must be considered when experimental electron-impact ionization energies are interpreted. In Fig. 4, we summarize results of our calculations of IAEs for all the cluster sizes in the region in question ( $N \leq 10$ ) and slightly beyond (up to  $N = 13$ ). For a further insight, data obtained from all simulation strategies employed in this work and for both fitting formulas are included and compared with the experiment. Several observations are well apparent from Fig. 4. Firstly, classical MC simulations (red bullets and circles), performed for temperatures for which monomer evaporation from the neutral precursor can be neglected, meet the experimental limits for  $\text{Ar}_N$  IAEs at  $N \approx 5 - 6$ . Similar conclusion is also valid for zero-temperature, quantum anharmonic calculations (q-DMC, blue stepwise lines), for which the experimental IAEs are reproduced for the first time at  $N \approx 5 - 6$ . The situation is even more favorable for the harmonic approximation calculations (q-HA, green stepwise lines), for which theoretical estimates of IAEs obtained via Eq. 1, i.e., that used in Ref. 5, lie significantly below the experimental points for all the cluster sizes considered. As mentioned above, this is a mere artifact of the harmonic approximation approach and cannot be considered a reliable prediction. Secondly, the classical Monte Carlo simulations yield, in general, IAEs which decrease rapidly if the cluster temperature increases. This is not surprising and can be easily understood by recalling the above discussion concerning Fig. 3. Namely, regions of the cluster configuration space with higher internal energies are sampled at higher temperatures and, consequently, the c-MC arrow of Fig. 3 climbs the repulsive wall of the neutral PES and moves to the left. This inevitably leads to a significant decrease of the IAE with increasing temperature. Thirdly, for the largest cluster sizes considered in Fig. 4 ( $N \geq 10$ ) and higher temperatures ( $T \geq 30 - 35$  K) the monotonous decrease of IAEs with rising temperature is corrupted. A natural explanation of this behavior is due to a solid-liquid phase change occurring in the neutral argon clusters for these sizes. The phase changes are also well apparent on corresponding heat capacity profiles as more or less pronounced

maxima occurring at temperatures about  $T \approx 30 - 35$  K as follows from our calculations [32] as well as from previous studies (see, e.g., Refs. 33–35). Note also, that the solid-liquid transition temperatures are rather close to the evaporative temperatures ( $T \approx 40 - 50$  K for  $\text{Ar}_{10} - \text{Ar}_{13}$  [32]) and compare well with experimental estimates of neutral argon clusters temperatures ( $T \approx 30 - 45$  K) as given, e.g., in Fig. 1 of Ref. [36].

#### IV. CONCLUSIONS

Calculations of vertical ion appearance energies (IAEs) of argon clusters have been performed for cluster sizes  $N = 3 - 13$  and compared thoroughly with a recent, state-of-the-art experiment [5]. The experimental conditions have been modeled by considering neutral clusters with distorted geometries (delocalized in the cluster configuration space), either due to thermal excitations (canonical parallel-tempering Monte Carlo methods) or by zero-point vibrations (sampling from harmonic vibration wavefunctions or fully anharmonic importance sampling diffusion Monte Carlo simulations). The main issue addressed in this work is an unexpected behavior of experimental electron-impact data supporting, for cluster sizes  $N \leq 10$ , the production of ionic clusters at electron energies considerably lower than theoretical estimates of vertical ionization potentials. Originally, this was interpreted in terms of the autoionization via highly excited Rydberg states of the neutrals [5, 10]. In this work, it has been demonstrated that structural distortions of neutral precursors, either due to thermal excitations or quantum zero-point vibrations, can shift the theoretical predictions of IAEs considerably closer to the experimental values. Except for the smallest cluster sizes,  $N = 3$  and 4, quantum zero-point vibrations can account for the experimentally observed IAEs even for frozen neutral clusters ( $T = 0$  K). For  $\text{Ar}_3$  and  $\text{Ar}_4$ , the discrepancy between experimental and theoretical IAEs still survives even if the delocalized structures are considered, which seems to indicate that both mechanisms, autoionization through Rydberg states proposed in Ref. 5 as well as cluster structure distortions discussed in this work, play a role [37]. It is further clear from our calculations that classical Monte Carlo IAEs coincide with the quantum predictions only for the highest temperatures considered in this work, i.e. for temperatures at which evaporation phenomena become pronounced. This complies well with recent findings based on path-integral Monte Carlo simulations on  $\text{Ar}_3$  [38].

Despite the fact that the present approach improves considerably theoretical estimates of

argon clusters IAEs, there still remain some open questions. More specifically, the evolution of experimental IAEs with the cluster size is qualitatively different from theoretical predictions. Whereas the theoretical values decrease quite rapidly with cluster size, experimental IAEs remain almost constant. A possible explanation of this effect is that excited electronic states of ionic daughters ( $\text{Ar}_N^+$ ) are involved. Conclusive answer to this question will require additional computations, however, which are postponed to a future work.

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- [37] Another explanation of the still surviving discrepancy between the theory and experiment for the smallest cluster sizes may be based on considering the fast fragmentation of argon clusters, which immediately follows their ionization. This means that experimentally observed ions may result, even at the ionization threshold, from a series of fast fragmentation (mostly monomer evaporation) steps rather than directly from the initial ionization event. Indeed, simple energetic considerations seem to support this idea. For example, theoretical estimates of the IAEs obtained from DMC calculations for  $\text{Ar}_5$  (15.005 eV) and  $\text{Ar}_6$  (14.967 eV) compare very well with the experimental IAEs reported for  $\text{Ar}_3$  (14.909 – 15.009 eV). Moreover, the internal energies of corresponding ions,  $\text{Ar}_5^+$  and  $\text{Ar}_6^+$ , are for configurations leading to VIPs close to fitted IAEs much higher than the energy of equilibrium  $\text{Ar}_3^+$  (by about +0.75 eV for  $\text{Ar}_5^+$  and +0.68 eV for  $\text{Ar}_6^+$ ). Consequently, the experimentally observed ionic trimers may originate from  $\text{Ar}_N^+ \rightarrow \text{Ar}_3^+ + (N - 3)\text{Ar}$ ,  $N \geq 5$ . Similar reasoning should also be valid for the tetramer and larger cluster sizes. However, the dynamics of post-ionization fragmentation of rare-gas clusters is extremely involved and still not well understood [8, 9, 39, 40], and much more work and simulations will be required to get a final answer.
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## Figures

Fig. 1

Experimental electron-impact ( $\bullet$ ) [5] and TPEPICO ( $\circ$ ) [4] ion appearance energies of  $\text{Ar}_N^+$  compared with classical adiabatic ( $\text{AIP}_0$ ) and vertical ( $\text{VIP}_0$ ) ionization potentials of  $\text{Ar}_N$  obtained from Eq. 1 for the N[2]I[dsi] interaction model and with the zero-point energy included (thick stepwise lines:  $\text{AIP}_0$  – gray,  $\text{VIP}_0$  – red). For comparison,  $\text{VIP}_0$  calculated for the N[2]I[d] and N[2]I[ds] models are also shown (green dotted line and blue dotted line, respectively) as well as the vertical ionization potential calculated for the N[2]I[dsi] model but with the zero-point energy of  $\text{Ar}_N$  not included ( $\text{VIP}_e$ , red dotted line).

Fig. 2

Dependence of the ionic signal for  $\text{Ar}_7 \xrightarrow{e^-} \text{Ar}_7^+ + e^-$  on the impact energy as calculated for the N[2]I[dsi] model and various sampling methods: q-HA – quantum sampling at  $T = 0$  K using the harmonic approximation (green dotted line), q-DMC – fully anharmonic, importance sampling diffusion Monte Carlo calculation (blue solid line), and c-MC – classical parallel-tempering Monte Carlo simulations at various temperatures (red lines, solid:  $T = 10$  K, dashed:  $T = 20$  K, dash-dotted:  $T = 30$  K, and dotted:  $T = 40$  K).

Fig. 3

A schematic sketch of the PES of neutral ( $\text{Ar}_N$ ) and ionic ( $\text{Ar}_N^+$ ) argon clusters (harmonic approximation to the  $\text{Ar}_N$  potential depicted as dotted curve) with typical ion appearance energies obtained for a given internal energy of the cluster (ZPE here) and various theoretical approaches included as upward arrows:  $\text{VIP}_0$  – classical zero-temperature calculation for the classical equilibrium geometry of the neutral an with the ZPE included, c-IAE – classical non-zero temperature Monte Carlo simulations, and q-IAE – zero-temperature quantum calculations either at the harmonic approximation level (green dotted arrow) or using the fully anharmonic, diffusion Monte Carlo approach (blue solid arrow).

Fig. 4

Ion appearance energies for the vertical ionization of  $\text{Ar}_N$  obtained for the N[2]I[dsi] interaction model, various simulation approaches and fitting strategies, and compared with experimental data [5] ( $\bullet$ ):  $\text{VIP}_0$  (gray solid line), q-HA + Eq. 2 (green solid line), q-HA +

Eq. 3 (green dotted line), q-DMC + Eq. 2 (blue solid line), q-DMC + Eq. 3 (blue dotted line), c-MC + Eq. 2 (red bullets), c-MC + Eq. 3 (red circles). Each point of the c-MC data corresponds to one particular temperature between  $T_{\min} = 5$  K and  $T_{\max}$  ( $T_{\max} = 25$  K for  $N = 3$  and 4,  $T_{\max} = 30$  K for  $N = 5$  and 6,  $T_{\max} = 35$  K for  $N = 7 - 9$ ,  $T_{\max} = 40$  K for  $N = 10$ ,  $T_{\max} = 45$  K for  $N = 11$  and 12, and  $T_{\max} = 50$  K for  $N = 13$ ) and with temperature increasing by  $\Delta T = 5$  K from the left to the right.

FIG. 1: See attachments.



FIG. 2: See attachments.

FIG. 3: See attachments.

FIG. 4: See attachments.

## Tables

TABLE I: Ion appearance energies (eV) obtained by fitting Eqs. 2 and 3 on the theoretical ion signal profiles of Fig. 2. The temperature at which evaporation of monomers emerges for Ar<sub>7</sub> has been estimated to  $T \approx 35 - 40$  K from our c-MC calculations.

ion signal	$E_0$	
	Eq. 2	Eq. 3
q-HA	$14.716 \pm 0.065$	$14.796 \pm 0.021$
q-DMC	$14.853 \pm 0.038$	$14.896 \pm 0.066$
c-MC (10 K)	$15.010 \pm 0.003$	$15.027 \pm 0.020$
c-MC (35 K)	$14.850 \pm 0.003$	$14.891 \pm 0.011$
exp. [5]	$14.869 \pm 0.050$	–

TABLE II: Classical ( $D_e$ ) and quantum ( $D_0^{(\text{HA})}$  and  $D_0^{(\text{DMC})}$ ) dissociation energies of small  $\text{Ar}_N$  clusters calculated either at the harmonic approximation (HA) level or in fully anharmonic diffusion Monte Carlo (DMC) calculations. All energies are given in meV. Compare also the energy obtained for  $\text{Ar}_3$  from the DMC calculation with the exact hyperspherical expansion value of Ref. 21,  $D_0 = 31.602$  meV.

$N$	$D_e$	$D_0^{(\text{HA})}$	$D_0^{(\text{DMC})}$
3	37.0	31.3	31.6
4	74.1	62.8	63.3
5	112.0	95.3	96.0
6	154.9	132.0	133.0
7	201.7	172.8	173.9









