

# Modelling of $\text{Kr}_n^+$ clusters IV: Structural changes in $\text{Kr}_3^+$ and $\text{Kr}_4^+$

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## Abstract

Constant-energy and constant-temperature Monte Carlo simulations have been performed to get insight into temperature-dependent structural changes taking place in the smallest krypton cluster cations,  $\text{Kr}_3^+$  and  $\text{Kr}_4^+$ . It is well known that trimers and tetramers form ionic cores of larger rare-gas cluster cations. The two smallest ionic clusters of krypton are thus used to analyze possible structural changes occurring in ionic cores of larger  $\text{Kr}_n^+$  clusters. The intra-cluster interactions are described using previously developed *diatomics-in-molecules* models for the  $\text{Kr}_n^+$  clusters with the inclusion of the spin–orbit coupling and the most important three-body non-additivities.

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## 1. Introduction

The rare-gas cluster cations are very attractive objects of study for both experimentalists and theoreticians. From the experimental point of view, they can be easily prepared, size-selected, manipulated, and, finally, detected; the attractiveness for theoreticians consists mainly in a possibility to model fairly complex processes occurring in these systems, including non-adiabatic or spin–orbit coupling effects, in a relatively simple way. Consequently, a lot of attention has been paid to the rare-gas cluster cations during the last 20 years and many challenging questions regarding their geometric and electronic structure, absorption of electromagnetic radiation, as well as dynamics have been solved by a common effort of experimentalists and theoreticians [1]. Several problems, however, still remain unsolved for these very interesting species. For example, a detailed knowledge of how the geometric and electronic

structure of the rare-gas cluster cations depends on their internal energy and/or temperature is of particular importance for the understanding and interpretation of their experimental photoabsorption spectra (see, e.g., Refs. [2,3]) as well as for getting a deeper insight into observed photofragmentation patterns ([4]). Despite the importance of the subject, there are presently available neither theoretical nor experimental studies on this interesting issue, at least to our knowledge. Recently, a series of studies have been published on the krypton cluster cations addressing a broad range of physico-chemical properties of these complexes, including intra-cluster interactions and structures [5], photoabsorption spectra [2,6], and photodissociation dynamics [7]. In the light of what is said above, a thorough investigation of thermodynamical properties of ionic clusters of krypton is highly desirable and the present article represents a first attempt to extend the previously published studies in this direction.

Structural (or phase) changes in clusters have been representing a rapidly developing branch of cluster science [8]. There are many reasons for this fact, the most important being probably the following ones: (1) the phase changes

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in clusters are completely different from those observed in the bulk and there is no smooth approach to the bulk limit for smaller cluster sizes; (2) the phase changes in finite-size systems are not sharp – there are coexistence regions on the temperature scale within which two or more phases may coexist; (3) the variety of the phase changes in clusters is much broader than those in the bulk (including pre-melting phenomena, surface melting, etc.); and, finally (4) certain peculiar phenomena can be encountered in clusters such as negative heat-capacities which were first observed in molecular dynamics calculations [9] and later on also experimentally [10,11]. One of the most powerful theoretical tools for getting a deeper insight into the nature of phase changes in clusters (and also into cluster thermodynamics in general) are computer simulations. Both molecular dynamics and Monte Carlo methods have been frequently used to study clusters of various chemical compositions and sizes, and there is a vast literature on both fundamental questions regarding thermodynamic simulations of finite-size systems and applications.

A lot of theoretical work on phase changes in clusters has been done for neutral homogeneous rare-gas (argon) clusters [12]. The rare-gas clusters are easy to model and are often considered a model laboratory for more complex systems. One would naturally expect that the phase changes in homogeneous rare-gas cluster cations should also be of particular interest, mainly because of the fact that the presence of positive charge transforms these species, although made of identical atoms, into heterogeneous systems. The positive charge localizes on a small subunit (ionic core), involving 2–4 atoms, surrounded by a cloud of almost neutral atoms. As the forces acting within the ionic core differ by an order of magnitude from the forces keeping together neutral atoms in solvation shells, one can anticipate that new phenomena may emerge during the structural changes in these systems, including, e.g., separate structural transformations of strongly bound ionic cores and in weakly bound neutral solvation shells. Unfortunately, no thermodynamical simulations have been reported for the rare-gas cluster cations so far. The present paper is a first attempt to fill this gap.

A series of thermodynamic simulations of krypton trimer and tetramer cations,  $\text{Kr}_3^+$  and  $\text{Kr}_4^+$ , are reported for a wide range of cluster internal energies and/or temperatures. The main focus is on the changes in the cluster structure, including the transformations of the delocalization of the positive charge as the cluster internal energy and/or temperature increases. This issue is of particular importance for the modelling of temperature dependence of  $\text{Kr}_n^+$  photoabsorption spectra as well as photofragmentation patterns. Monte Carlo methods have been employed in our simulations using both microcanonical and canonical samplings to visualize differences between the most commonly employed statistical ensembles. Several previously developed interaction models based on the *diatomics-in-molecules* approach have been used to assess how

uncertainties in the interaction models affect the simulation data.

The paper is organized as follows: first, a brief survey of the interaction models, simulation techniques, and thermodynamical and structural parameters used in our calculations is given in Section 2, then, simulation data are presented and discussed briefly in Section 3, and, finally, major achievements are summarized in Section 4.

## 2. Methods and computations

### 2.1. Interaction models

Several previously developed models [5] based on the *diatomics-in-molecules* approach [13] have been used to describe the intra-cluster interactions in the  $\text{Kr}_n^+$  clusters: the original model by Kuntz and Valldorf [14], and its two principal extensions including the spin–orbit coupling and the most important three-body polarization interactions. The spin–orbit coupling is rather strong in heavy krypton atoms and cannot be neglected even for the smallest cluster sizes. How to include it in the original *diatomics-in-molecules* model is shown in Ref. [15]. Even though the three-body polarization interactions are particularly important for larger cluster sizes, they can also lead to well observable effects in the smallest rare-gas cluster cations (e.g., to a change in the equilibrium geometry of  $\text{Kr}_4^+$ , see Table 2). They can be included in the *diatomics-in-molecules* model through semiempirical schemes introduced in Ref. [15].

A detailed description of the models employed in the present calculations can be found in the first paper of this series [5] or in Ref. [16], thus only a brief survey of the models will be given here (together with abbreviations used throughout this work): DIM – the original *diatomics-in-molecules* model by Kuntz and Valldorf [14], DIM + SO – the DIM model with the inclusion of the spin–orbit coupling, and DIM + SO + ID – ID – the DIM model with the inclusion of both the spin–orbit coupling and the leading three-body polarization terms of the induced dipole – induced dipole type.

All the interaction models introduced above require several independent inputs which must be supplied either from independent (ab initio) calculations or from experiment: the diatomic interaction curves for the electronic ground state and the first three excited states of the krypton dimer cation,  $\text{Kr}_2^+$ , the potential energy curve for the electronic ground state of the neutral krypton dimer,  $\text{Kr}_2$ , the fine-structure (spin–orbit) splitting of the electronic ground state of the krypton cation,  $\text{Kr}^+$ , and the static polarizability of the krypton atom. In our modellings, the diatomic interaction curves have been taken from extensive ab initio calculations for  $\text{Kr}_2^+$  [5] and from semiempirical modellings for  $\text{Kr}_2$  [17]. The fine-structure splitting between the  $^2\text{P}_{1/2}$  and  $^2\text{P}_{3/2}$  states of  $\text{Kr}^+$  ( $5370.1 \text{ cm}^{-1}$ ) is taken from Ref. [18], and the krypton polarizability volume ( $17.075 \text{ bohr}^3$ ) from Ref. [19].

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