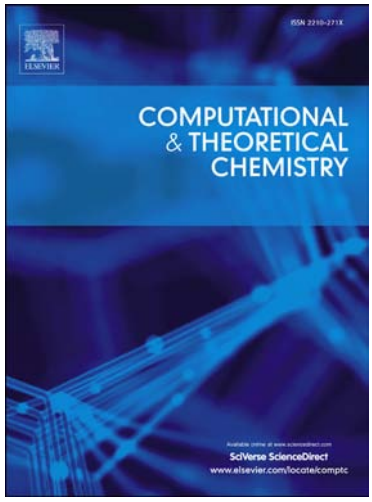


Structures, relative stabilities, and electronic properties of potassium clusters $K_n$ ( $13 \leq n \leq 80$ )

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# Structures, relative stabilities, and electronic properties of potassium clusters $K_n$ ($13 \leq n \leq 80$)

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**Abstract**

We report the global minimum (GM) structures, energetic and electronic properties of $K_n$ clusters with up to 80 atoms, obtained by combining basin hopping unbiased optimizations (based on a many-body empirical potential) with subsequent reoptimization of several candidate structures employing a density functional theory method which accounts for van der Waals dispersion interactions (vdW-DFT). A comparison with other alkali cluster systems shows that the GM structures of $K_n$ coincide with those of $Na_n$ more often than with those of $Cs_n$ clusters. Nevertheless, the inclusion of dispersion interactions produces for several clusters changes in the GM structures, which become either identical to those of $Cs_n$ clusters, or completely novel (i.e. not reported for other alkali systems). Many GM structures are based on poly-icosahedral packing; some others contain Kasper polyhedral units with disclination lines. Atoms with a low coordination number (or adatoms) are avoided in the GM structures following a geometric shell closing: such additional atom is instead inserted into the outermost atomic shell of the cluster. The calculated ionization potentials, electron affinities and HOMO-LUMO gaps are found to reproduce perfectly the electron shell closings observed in photoionization measurements. The electric dipole moments of most clusters are close to zero, a distinguishing feature of metallicity previously observed for $Na_n$ clusters. However, some clusters like $K_{26}$, $K_{47}$ or $K_{49}$ have sizable electric dipole moments. The cluster stabilities are found to explain the experimental abundances inferred from mass spectra. The enhanced stabilities (magic numbers) can be interpreted in terms of electron shell closing effects for the smaller clusters and of geometrical packing effects for the larger clusters. Although there is not a sharply defined critical size separating both regimes, it is estimated to be around 55 atoms.

*Keywords:* Potassium clusters, Density Functional Theory, van der Waals interactions, Magic clusters, Global optimization, Basin Hopping, Cluster Structure, Ionization Potential

## 1. Introduction

There has been an ongoing interest during last years in understanding the geometric packing preferences of small atomic clusters. Together with the electronic structure, cluster geometry determines several physical and chemical properties such as reactivity, optical absorption, etc, which are of general interest in Nanoscience. Typically, the structure and other cluster properties can differ substantially from those of isolated molecules and macroscopic systems, due to quantum confinement effects on the electron cloud and also to the large proportion of surface atoms. Alkali metal clusters were amongst the first nanoscopic systems investigated with mass spectroscopic techniques (1). Those seminal studies revealed that clusters with 8, 20, 34, 40, 58,... electrons have an enhanced stability as compared to other cluster sizes. The magic sizes were understood in terms of a well defined electron shell structure with the help of the structureless jellium model (2, 3). Since then, alkali clusters have remained an interesting object of study because they are representative of simple metal clusters with delocalized electrons. In particular, first principles methods such as quantum chemistry methods and density functional theory have been applied to study many structural, thermal, electronic and optical properties of sodium clusters (4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31), contributing much to our present understanding of the

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