

Intermolecular interactions and stability of cationic alkali-dimers in He clusters

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Synopsis Doped He droplets constitute an important environment as ultracold homogeneous matrices for spectroscopic studies. Alkali metal dopants have a series of interesting properties due to their unusual bonding behavior. Neutral atoms attached to the surface of the droplet, forming eventually cold molecules via collisions, while charged dopants form solvation shells, related with the low mobility of the ions in experiments. So, investigations on the underlying intermolecular, markedly orientational ionic, forces, and on the microscopic structures of alkali-cation-He complexes is essential.

We present a detailed theoretical investigation on intermolecular interactions of cationic alkali-dimers solvated in small He clusters [1, 2]. The structural characteristics and stabilities of such cations are determined from high level *ab initio* electronic structure calculations. In particular, interaction energies are obtained from CCSD(T)/CBS and MRCI+Q calculations, depending on the single- or multi-reference character of the system under study. In turn, the potential energy surfaces are constructed employing an interpolation technique within the Reproducing Kernel Hilbert Space (RKHS) method, and were used to evaluate the trimers' nuclear quantum effects. By analyzing the potential anisotropy and the spatial arrangement of the ground and excited vibrational states, we found that energetically the most stable conformer corresponds to linear arrangements for all complexes studied.

Further, we have looked into the behavior of higher-order species with more He atoms surrounding the cationic dopant. A simplified sum of the three-body *ab initio*-based potential approach is employed to describe the microsolvation of the $A_2^+(^2\Sigma)$ molecular ions ($A=Li, Na, K, Cs,$ and Rb) in He clusters by analyzing the structural stability of clusters with up to six He atoms in comparison with interactions energies obtained from quantum chemistry methods [1].

The optimized structures are analyzed in terms of their geometric features, confirming the dominance of ionic forces in driving the shape of the cluster, and their crucial role by changing the competitive strength of the cation-He interaction with respect to the He-He (pure solvent) network of interactions. Such interplay creates collocations, like the equilateral He_3 motifs (see figure) at the two ends of each ionic dimer, that provides some initial information on solvation process at microscopic level.

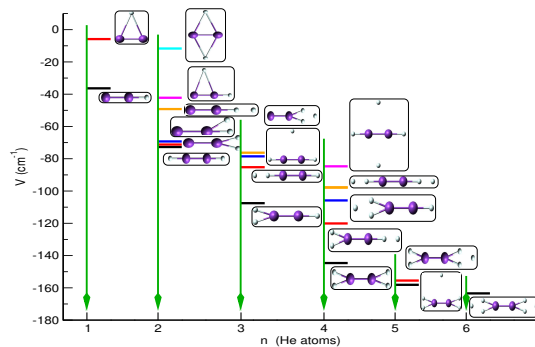


Figure 1. Optimal structures for the indicated $He_n-K_2^+$ clusters.

References

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