Theoretical study of the Na\textsuperscript{+}Kr\textsubscript{n} and NaKr\textsubscript{n} (n=1-25) small clusters

J. Dhiflaoui\textsuperscript{a}, H. Bouzouita\textsuperscript{a} and H. Berriche\textsuperscript{a,b,*}

\textsuperscript{a}Laboratoire de Physique et Chimie d’Interfaces, Département de Physique, Faculté des Sciences de Monastir, Avenue de l’Environnement, 5019 Monastir Tunisie

\textsuperscript{b} Physics Department, Faculty of Science, King Khalid University, P. O. B. 9004, Abha, Saudi Arabia.

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Abstract

We have studied the structure and the stability of the ionic Na\textsuperscript{+}Kr\textsubscript{n} and neutral NaKr\textsubscript{n} (n=1-25) small clusters. The potential energy surface of the cluster is described using additive potentials, which represent the pair interactions taken from the best available CCSD ab initio calculations. The V_{Na+Kr}, V_{Kr-Kr} potentials have been fitted, respectively, by Tang and Toennies and Lennard-Jones (LJ) forms, while the V_{NaKr} is presented by a modified HFD analytical potential obtained by a fully quantum-mechanical approach based on very accurate spectroscopic data. In addition, the potential energy surface has been explored by the Monte Carlo Basin Hopping method in order to determine the geometry of Na\textsuperscript{+}Kr\textsubscript{n} and NaKr\textsubscript{n} clusters and their isomers.

Their relative stability was studied by evaluating the energy per Krypton atom and the energy differences as function of number n of Krypton atoms in clusters. It was shown, for Na\textsuperscript{+}Kr\textsubscript{n}, that n = 6, 8, 10, 16 and 20 are the most stable structures, which is in good agreement with the previous experimental results.

1. Introduction

The experimental and theoretical structures of the atomic and molecular clusters have been an interesting subject for several years. Their interest stems in understanding the properties of the system from small size to the macroscopic states. However, it was soon discovered that clusters might have their own importance since they present properties, which are not encountered either in the monomers or in the macroscopic state. Several works [1-10] have been done on alkali atoms and alkali ions in a rare gas cluster or matrix. Froudakis et al [11] have studied Li\textsuperscript{+}Rg\textsubscript{n} (Rg = Ne, Ar and Kr) clusters by mass spectroscopic techniques and by theoretical modeling. They have determined the lowest minimum energy structures and have shown that the first closed shell geometries are
octahedral. In a recent work [12], we have studied the Na+Ar_n small clusters and we have determined their equilibrium structure. Such geometries were used to investigate the excited states of the neutral NaAr_n clusters. Clusters involving alkali ions, such as sodium and potassium, were among the first studied systems due to the simplicity of the electronic configuration of the alkali atoms. It was demonstrated that the noble gas atoms tend to a geometrical arrangement around the alkali ion. Such arrangement has been observed for several X'Rg_n (X' = Li, Na) clusters and has been well explained previously [13-14]. There also exists other work introducing alkali ion interacting with Argon clusters such as M'Ar_n (M = Li, Na, K) [12] clusters. Lüder et al [15] have studied the In'Rg_n, Al'Rg_n, and Na'Rg_n (Rg= Ar, Kr, Xe) clusters. In a recent work, we have studied the Na'+Krn (n = 1, 20) small clusters [16] and we have determined their equilibrium structures. For our best knowledge there are no studies on NaKrn neutral clusters. The purpose of this work is to investigate the interaction of Na+ and Na with small Kr_n clusters for n = 1 to 25.

We use a simple model for the Na'+Kr_n and NaKrn clusters, where the potential energy surface is constructed by adding the different Na'+Kr and Kr_2 and NaKr pair potentials. For this aim we have interpolated the Na'+Kr and Kr-Kr potentials taken, respectively, from the recent and accurate CCSD calculations of Viehland et al [17] and Slavicek et al [18]. We have used for the Na'+Kr potential the analytical form of Tang and Toennies [19] and for the Kr_2 potential the Lennard-Jones (LJ) form. The NaKr interaction was taken from the work of Brühl et al [21] in its modified HFD form extracted from accurate laser spectroscopic investigation of the A-X spectral intensity distribution of the fluorescence light.

Our paper is organized in the following way: section 2 contains the method of calculation; in section 3 we present our results for the Na'+Krn and NaKrn small cluster. Finally we conclude.

2. Method of calculation

The total potential energy of Na'+Kr_n clusters is assumed to be an additive potential composed from Na'+Kr and Kr-Kr interactions. In this context, the total potential energy is given by:

\[ V(R) = \sum_{i=1}^{n} V_{Na^+Kr_i}(R) + \sum_{i=1}^{n} \sum_{i<j}^{n} V_{Kr-Kr}(R) \]

(1)

where the first and the second terms present, respectively, the alkali-noble gas and the noble gas-noble gas interactions. They are, respectively, taken from the recent and accurate CCSD calculations of Viehland et al [17] for Na'+Kr and Slavicek et al [18] for Kr-Kr. We used the analytic potential form given by Tang and Toennies [19] to describe the Na'+Kr interaction. However, a Lennard Jones (LJ) potential has been employed [19] for the weak interaction between rare gases atoms.

The analytic potential of Tang and Toennies has the following form:

\[ V_{Na^+Kr}(R) = A_{eff}\exp(-bR) - \frac{D_4}{R^4} - \frac{D_6}{R^6} - \frac{D_8}{R^8} - \frac{D_{10}}{R^{10}} \]

(2)

The parameters A_{eff}, b, D_4, D_6, D_8 and D_{10} are obtained by a square fitting using the potentials of Viehland et al [19]. They have used an accurate Coupled Cluster Simple and Double excitation (CCSD(T)) calculation. In this case, the equilibrium distance R_e and the well depth D_e are respectively 5.52 a. u and 1689 cm^{-1}. The fitted parameters for Na'+Kr using the analytical form of Tang and Toennies are summarized in table 1. Fig. 1 presents of the total potential compared to the numerical potential used in the fitting. The difference between the analytical potential containing all terms and the numerical one doesn’t exceed 10^{-5} a. u. corresponding to less than 3 cm^{-1}.

For the Kr_2 dimer, we have used the analytical potential form of Lennard Jones [20]:
\[ V_{Kr-Kr}(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \right] \]  

(3)

Where \( \varepsilon \) and \( \frac{\sigma}{2^{1/6}} \) represent, respectively, the well depth and the equilibrium distance of the Kr\(_2\). We obtain the values \( \varepsilon = 0.6050810^{-3} \) a. u. and \( \sigma = 6.8375 \) a. u.

In Fig. 2 we present LJ potential [20] and the numerical potential of Slaviceck et al [18] for Kr\(_2\). We remark a very good agreement between the two potentials and, as the last case, the difference between the analytical and the numerical potentials doesn’t exceed few cm\(^{-1}\).

**Table 1**: Interpolation parameters (in a. u.) of Na’Kr interaction

<table>
<thead>
<tr>
<th>A(_{eff})</th>
<th>b</th>
<th>D(_4)</th>
<th>D(_6)</th>
<th>D(_8)</th>
<th>D(_10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170.137</td>
<td>1.82343</td>
<td>8.03434</td>
<td>160.631</td>
<td>605.664</td>
<td>-2726.29</td>
</tr>
</tbody>
</table>

For the NaKr\(_n\) cluster, we have used also an additive potential composed from NaKr and Kr-Kr interactions, in this context the total potential is given as follow:

\[
V(R) = \sum_{i=1}^{n} V_{NaKR}(R) + \sum_{i=1}^{n} \sum_{j<i} V_{Kr-Kr}(R)
\]

(4)

Where the first term represents the interaction between alkali and the Krypton atoms. To describe this interaction we have used the analytical form of the Hartree-Fock-Dispersion (HFD) potential. Different variants of the HFD potential exist in the literature. In this work we use the so called HFD-A form [21],

\[
U(R) = Ae^{-\alpha R} - \left( \frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} \right) F(x) + T_0
\]

(5)
F(x) is a damping function and TD is the dissociation limit.

\[
F(x) = \begin{cases} 
\exp\left(-\left(\frac{D}{x} - 1\right)^2\right) & x < D \\
1 & x \geq D
\end{cases}
\]

(6)

Where \(x = R/R_m\) is a scaling parameter and is not identical to the equilibrium distance. The form of the HFD potential is similar to that of the Tang and Toennies potential, the main modification being the different choice of the damping function F(x). The parameters of HFD potential are given by Brühl et al [21] (see table 2).

<table>
<thead>
<tr>
<th>n</th>
<th>D</th>
<th>R_m (Å)</th>
<th>A (cm⁻¹)</th>
<th>α</th>
<th>10⁶ C₆</th>
<th>10⁻⁶ C₈</th>
<th>10⁻⁸ C₁₀</th>
<th>TD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.35</td>
<td>4.72401</td>
<td>1.384201</td>
<td>10.42</td>
<td>3.72349</td>
<td>-9.63372</td>
<td>11.81725</td>
<td>61.32</td>
</tr>
</tbody>
</table>

The potential energy surface is then explored by the Basin Hopping method. This global optimization approach was developed first by Wales and Doye [22]. This method uses the energy minimization and the Monte Carlo technique. The potential energy is transformed to a new surface which has the form of multidimensional staircase. The steps correspond to the basins of attraction contains the set of configuration which after geometry optimization generate a particular minimum. The basin hopping method is very powerful and has been used in many works. A detailed description can be found in the reference [22].

3. Results and discussion

3.1. Structure and stability of the Na⁺Krₙ (n = 1 - 25) ionic clusters

To find the geometry corresponding to the lowest energy, we use the powerful global optimization Basin Hopping method. Using such Monte Carlo technique, the geometry and the lowest-energy of the Na⁺Krₙ (n = 1-25) small clusters have been determined. The obtained structures are presented in Fig. 3

The first step in our calculation is to test the optimization procedure for the Na⁺Kr van der Waals system. We find an equilibrium distance of 5.51 a. u. and a well depth 1691.768 cm⁻¹ which are in excellent accord with the used numerical potential. Na⁺Kr₂ complex is found to have a triangular structure with Na⁺ ion on the summit; the Na⁺Kr bonds are 5.51 a. u., while Kr-Kr bonds is 7.67 a. u. The Na⁺Kr₂ cluster has a tetrahedron structure. Na⁺Kr₃ has a square pyramid structure with the Na⁺ ion in the centre. The Na⁺Kr₄ is obtained by addition a Krypton atom to the Na⁺Kr₃, which leads to a bi-pyramidal high symmetry structure. Similarly, the Na⁺Kr₅ structure is obtained by adding a Krypton atom to the Na⁺Kr₄ cluster.

The isomers appears from n=10. We found two isomers for Na⁺Kr₁₁, Na⁺Kr₁₂ and Na⁺Kr₁₆, while three isomers are found for Na⁺Kr₁₀, Na⁺Kr₁₃, Na⁺Kr₁₄, Na⁺Kr₁₅, Na⁺Kr₁₆, Na⁺Kr₁₇, Na⁺Kr₁₈ and Na⁺Kr₂₀ clusters. The geometrical structure and the energies of such isomers are given in Figure 3. For n>23 we present only the cluster having the lowest energy.

To study the stability of Na⁺Krₙ clusters, we present in Fig. 4 (a) the binding energy per atoms of Krypton e(n) = -E(n)/n. We remark that Na⁺Kr₉ correspond to the most stable cluster. For a better understanding of the relative stability of Na⁺Krₙ clusters, we have evaluated the first derivative ΔE = E(n+1) - E(n). Such quantity is plotted on Fig. 4 (b), which reveals the stability of n = 6, 8, 10, 12, 16 and 20 clusters. Finally, to study the stability of Na⁺Krₙ clusters in more details, we have calculated the second derivative of the cluster size n, which is defined as: Δ²E = E(n-1) + E(n+1) - 2E(n). This quantity is a general measure of the relative stability and can be compared directly with the mass spectra experiment. As it is shown on Fig. 4 (c), we obtain n = 6, 8, 9, 10, 12, 16 and 20 as magic numbers. However, only n = 6, 8, 10, 16, and 20 presents significant intensity in contrast to that related to n = 9 and
12, which reveals that relatively stable complex are formed for 6, 8, 10, 16, 20. These magic numbers are in excellent agreement with the experimental TOF-Spectra of Lüder et al [15].

In order to explain the obtained magic numbers observed in Fig. 4 (c), we apply a simple geometrical model of hard sphere packing [23]. In this model we suppose that the dopant Na⁺ resides in the center of the cluster and is surrounded by n noble gas atoms. An important condition has to be fulfilled to obtain stable clusters by applying the hard sphere model. This condition states that the distance $d_M$ of the central atom and the distance $d_s$ between two noble gas atoms have the following relation:

$$ R^* = \frac{d_M}{d_s} \leq 0.5 \left[ \frac{(2 + \cos\left(\frac{\pi}{k}\right) - \cos\left(\frac{2\pi}{k}\right))}{(1 - \cos\left(\frac{2\pi}{k}\right))} \right]^{1/2} $$

(7)

With $k = n/2$ represents the numbers of atoms per ring. That is, we obtain the maximum $R^*$ values for $k = 2$ to 5 so that for $0.82266 \leq R^* \leq 0.951$ icosahedral packing is preferred, for $0.707 \leq R^* \leq 0.82266$ CSA (Capped Square Antiprism: CSA) packing, for $0.6125 \leq R^* \leq 0.707$ octahedral packing and for $R^* \leq 0.6125$ tetrahedral packing. In Table 3, we present $d_{Na^+Kr}$, $d_{Kr-Kr}$ and $R^*$ for Na⁺Kr₆, Na⁺Kr₈ and Na⁺Kr₁₀ clusters. This table illustrates that Na⁺Kr₆, Na⁺Kr₈ and Na⁺Kr₁₀ have, respectively, an octahedron, a square antiprism (SA) and a Capped Square Antiprism (CSA) packing.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>$d_{Na^+Kr}$</th>
<th>$d_{Kr-Kr}$</th>
<th>$R^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 6</td>
<td>5.488</td>
<td>7.76</td>
<td>0.707</td>
</tr>
<tr>
<td>n = 8</td>
<td>5.84</td>
<td>7.10</td>
<td>0.822</td>
</tr>
<tr>
<td>n = 10</td>
<td>5.85</td>
<td>7.13</td>
<td>0.820</td>
</tr>
</tbody>
</table>

**Structure and energy of the NaKrₙ (n = 1- 25) neutral clusters:**

For the NaKrₙ neutral small clusters (n = 1-25), we observe a fundamental difference with the geometry of the Na⁺Krₙ ionic clusters. We can assume that the ion Na⁺ is confined in the center of the Na⁺Krₙ cluster and is surrounded by the n krypton atoms, while the Na atom is on the surface of the neutral cluster. This can be explained by the difference of the binding energies of Na⁺Kr, Kr-Kr and NaKr. These energies decrease from Na⁺Kr to NaKr. Furthermore, the bond length in the NaKr dimer, which is equal to 9.29 a. u, is much longer than that of the Na⁺Kr ionic one (5.52 a. u).

We remark that NaKr₃ has a triangular structure and the sodium atom occupies the summit. However, the NaKr₃ cluster has a pyramidal structure. In fact, the geometrical difference between Na⁺Krₙ and NaKrₙ clusters appears from n = 4 and becomes more important when the number of Krypton atoms n increases. The geometrical structure and the energies of the neutral NaKrₙ clusters and their isomers are given in Figure 5.

```
<table>
<thead>
<tr>
<th>n = 1 (-0.00769499848)</th>
<th>n = 2 (-0.0159950769)</th>
<th>n = 3 (-0.0249002354)</th>
<th>n = 4 (-0.0339365009)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 5 (-0.043563673)</td>
<td>n = 6 (-0.0537837473)</td>
<td>n = 7 (-0.0600961835)</td>
<td>n = 8 (-0.0667885271)</td>
</tr>
</tbody>
</table>
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Figure 3: Structure, isomers and energy (in a. u.) of Na⁺Krn (n = 1-25) Clusters

Figure 4: Binding energy per atom of Kr (a), the first derivative (b) and the second derivative (c).
<table>
<thead>
<tr>
<th>$n=1$</th>
<th>$n=2$</th>
<th>$n=3$</th>
<th>$n=4$</th>
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<tbody>
<tr>
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<td>(-1.91358034010^{-3})</td>
<td>(-3.505683717610^{-3})</td>
</tr>
<tr>
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<td>$n=7$</td>
<td>$n=8$</td>
</tr>
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<td>(-7.127753845510^{-3})</td>
<td>(-9.164029482110^{-3})</td>
<td>(-1.120266771710^{-2})</td>
</tr>
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<td>$n=10$</td>
<td>$n=10$</td>
<td>$n=11$</td>
</tr>
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<td>(-1.862775210^{-2})</td>
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<tr>
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<tr>
<td>$n=13$</td>
<td>$n=14$</td>
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<td>$n=15$</td>
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<td>(-3.158861710^{-2})</td>
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</table>
3. Conclusion

We have studied the structure and the stability of the ionic Na⁺Krₙ and neutral NaKrₙ (n = 1-25) small clusters using a pair additive Lennard-Jones and a Tang and Toennies and potential for Kr₂ and Na⁺Kr interactions. The two analytical forms were fitted from very accurate CCSD calculations of Viehland et al [17] for Na⁺Kr interaction and Slavisek et al for Kr₂ [18]. The VNaKr potential is presented by a modified HFD analytical potential obtained by a fully quantum-mechanical approach based on very accurate spectroscopic data. The derived potential energy surface of Na⁺Krₙ and NaKrₙ complexes has been explored by the Monte Carlo Basin Hopping method and the geometry of each Na⁺Krₙ and NaKrₙ cluster and its isomers was determined. The relative stability of the ionic clusters was studied by calculating the energy per Krypton atom, the first and the second derivatives. It was shown that n = 6, 8, 10, 16 and 20 correspond to the magic numbers related to the most, relatively, stable clusters. These numbers are in excellent agreement with the TOF-spectra of Lüder et al [15]. In addition, a simple hard sphere model was applied...
for the Na\(^{+}\)K\(_n\) clusters and has confirmed the obtained geometrical structures. The optimised structures for the neutral NaK\(_n\) clusters has revealed as expected the surface interaction of the sodium atom with the Kr\(_n\) cluster.

References