Theoretical study of the structures, stabilities, and electronic properties of Na$_2^+$Xe$_n$ ($n = 1$–6) clusters

Chedli Ghanmi, Mefteh Bouhalleb, Sameh Saidi, and Hamid Berriche

Abstract: The structures and stabilities of Na$_2^+$Xe$_n$ ($n = 1$–6) clusters are investigated using an accurate ab initio approach and an analytic potential form for the Na$^+$–Xe and Xe–Xe interactions. The potential energy surfaces of the Na$_2^+$($X^2\Sigma^+_g$)–Xe$_n$ ($n = 1$–6) clusters are performed for a fixed distance of Na$_2^+$($X^2\Sigma^+_g$) in its equilibrium distance. For $n = 1$, the potential energy surfaces have been computed for an extensive range of the remaining two Jacobi coordinates, $R$ and $\gamma$. In addition, we have determined the potential energy surfaces of 15 isomers of Na$_2^+$($X^2\Sigma^+_g$)–Xe$_n$ ($n = 1$–6). The potential energy surfaces are used to extract spectroscopic information on the stability of the Na$_2^+$($X^2\Sigma^+_g$)Xe$_n$ ($n = 1$–6) clusters. For each $n$, the stability of the different isomers is examined by comparing their potential energy surfaces. We find that the most stable isomers are C$_{\infty v}$(11), D$_{\infty h}$(21), C$_{2v}$(31), D$_{2h}$(41), C$_{3v}$(51), and D$_{3h}$(61). To our knowledge, there are no experimental and theoretical studies on the collision between the Na$_2^+$($X^2\Sigma^+_g$) alkali dimer and the xenon atom.

1. Introduction

During the past decade, embedding atoms and small molecules in rare gas clusters has been developed rapidly and become an important challenge on both experimental and theoretical sides. Special intense interest is paid to the study of the clusters involving helium and other noble gas atoms as components. The rare gas clusters, especially those involving helium atoms, represent an ideal testing ground for many computational approaches [1–5], because accurate knowledge of the relevant intermolecular forces between the solvent atoms and the dopants present in the cluster is an important prerequisite for the structural calculations and therefore fairly simple components provide ideal model systems for the analysis of the influence of intermolecular interactions on the clusters’ properties [6–8]. The structures and stability of atoms and diatomic molecules embedded in rare gas clusters have been extensively investigated by several experimental and theoretical works, because doped noble gas clusters present some additional interesting features, like the rapid heat transport generated inside the complex to the surface. Experimentally, Fuchs et al. [9] measured the total integral scattering cross sections for Li$_2$ molecules in selected rotational and vibrational states up to $v = 21$ in collision with the helium and krypton atoms. Recently, An der Lan et al. [10] achieved an experimental solvation of Na$^+$ and K$^+$ and their dimers in helium droplets. They found that Na$_2^+$He$_n$ displays two distinct anomalies at $n = 2$ and 6. Theoretically, numerous studies have been realized in the field of the interaction between neutral or ionic alkali molecules and a single noble gas atom, rare gas matrix, or droplets. In this context, Douady et al. [11, 12] performed a theoretical study of the Na$^+$ solvation in an argon matrix, Ar$_n$. They showed that the relatively strong interaction between the charged molecule and the Ar atoms favors trapping of the molecule inside the cluster rather than at the surface. Lately, ab initio computed interaction forces were employed by Marinetti et al. [13] to describe the microsolvation of the Li$_2^+$, Na$_2^+$, and K$^+$ molecular ions in the helium clusters of small variable size. Bodo et al. [14] determined, by Hartree–Fock quantum calculations, the structure and stability of the small Li$_2$–(He$_n$) clusters. More recently, Zanutti et al. [15] presented, using a theoretical approach based on core polarization pseudopotential, an investigation of the structure and optical absorption of Li$_2^+$, Na$_2^+$, and K$^+$ alkali dimers solved in Ne$_n$ clusters for $n = 1$ to a few tens of Ne atoms.
The aim of this paper is to extend our previous works [16, 17] on the Li_{2n}(X^{2S+}) alkali dimer in interaction with small Xe_{m} (n = 1–6) clusters. This paper is organized as follows. Section 2 outlines the computational methods used in this study. Section 3, which is separated into two parts, is devoted to presenting our results: the potential energy surfaces in different radial geometries and for six angles of the Na_{2n}(X^{2S+})Xe, and the structure and stability of small Na_{2n}(X^{2S+})Xe_{m} (n = 1–6) clusters. Section 4 summarizes our results with a conclusion.

2. Method of calculations

The potential energy surfaces, for the Na_{2n}(X^{2S+})Xe_{m} (n = 1–6) clusters are computed by fixing the Na_{2n}(X^{2S+}) alkali dimer at its equilibrium distance of 6.83 a.u. determined previously by Berriche [18]. As in our previous works [16, 17], the Na_{2n}(X^{2S+})Xe_{m} (n = 1–6) clusters are treated as a one-electron system using the non-empirical pseudopotential proposed by Barthelat et al. [19] in its semi-local form. The Gaussian-type orbital basis sets used for the sodium and xenon atoms are (7s6p5d/6s5p4d) and (4s3p), respectively. The cut-off radii used for s, p, and d orbitals are 1.4422, 1.625, and 1.5 a.u., respectively, for Na [7] and 3.500, 14.8, 4.0, and 1.401 a.u., respectively for Xe [20]. The core dipole polarizability of Na and Xe atoms are 0.993 [21] and 27.29 a.u., respectively [22]. The coredipolepolarizability of Na and Xe atoms are 0.993 [21] and 27.29 a.u., respectively [22].

Using the non-empirical pseudopotential proposed by Barthelat et al. [19], the two Na+ ions and the Xe atoms are treated as a core interacting only with the alkali valence electron. Based on this approach the total potential of the Na_{2n}(X^{2S+})Xe_{m} (n = 1–6) clusters is obtained as a sum of three contributions. In this context, the total potential is given by

\[ V_{\text{Tot}} = V_{e-Na_{2n}^{+}-Xe_{m}} + \sum_{i=1}^{n} V_{Na_{2n}^{+}-Xe_{i}} + \sum_{i=1}^{n} V_{Na_{2n}^{+}-Xe_{i}} \]

\[ + \sum_{i=1}^{n} \sum_{j>i}^{n} Xe_{i} - Xe_{j} \]

(1)

The first term represents the interaction between the valence electron and the ionic system Na_{2n}^{+}Xe_{m} (n = 1–6). The three other terms represent the core–core interactions and the noble gas – noble gas interactions.

For the \( V_{e-Na_{2n}^{+}-Xe_{m}} \) (n = 1–6) contribution, we performed a one-electron ab initio self-consistent field calculation where the two Na+ cores and the electron–xenon effects have been replaced by semi-local pseudopotentials [19].

The \( V_{Na_{2n}^{+}-Xe_{m}} \) contribution is taken from the accurate coupled cluster single and double excitation calculations of Lozzie et al. [23]. For a better representation of the Na+–Xe interaction in the region of interest for the Na_{2n}(X^{2S+})Xe_{m} system, the Na+–Xe numerical potential is fitted using the analytical form of Tang and Toennies [24]. Such potential contains the well-known long-range terms of van der Waals interactions and the usual exponential repulsive part. It is written as follows:

\[ V_{Na_{2n}^{+}-Xe} = A_{\text{eff}} \exp(-bR) - \frac{D_{4}}{R^{4}} - \frac{D_{6}}{R^{6}} - \frac{D_{8}}{R^{8}} - \frac{D_{10}}{R^{10}} \]

(2)

The parameters \( A_{\text{eff}}, b, D_{4}, D_{6}, D_{8} \) and \( D_{10} \) are obtained by a square fitting using the potentials of Lozzie et al. [22]. These parameters are presented in Table 1.

For the noble gas – noble gas interactions, we used the Lennard–Jones (LJ_{6–12}) analytical potential given by

\[ V(R) = 4\epsilon \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \]

(3)

Table 1. Interpolation parameters (in a.u.) of Na+Xe interaction.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>b</td>
<td>1.6605</td>
</tr>
<tr>
<td>( D_{4} )</td>
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</tr>
<tr>
<td>( D_{6} )</td>
<td>87.504</td>
</tr>
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<td>( D_{8} )</td>
<td>17479.9</td>
</tr>
<tr>
<td>( D_{10} )</td>
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</table>

Fig. 1. Coordinates of the Na_{2n}(X^{2S+})Xe used in the calculation.

where \( \epsilon \) and \( (2\sqrt{\epsilon}/\sigma) \) represent the well depth and the equilibrium distance of the Xe_{m} dimer, respectively, which are 0.000882 and 7.295 a.u., respectively [24].

For the Na_{2n}(X^{2S+})Xe_{m} cluster, the potential energy surfaces have been computed for an extensive range of the remaining two Jacobi coordinates, \( R \) and \( \gamma \). We reported in Fig. 1 a descriptive model of the coordinates of the Na_{2n}(X^{2S+})Xe_{m} cluster, where the distance \( R \) represents the separation between the xenon atom and the center-of-mass of the Na_{2n}(X^{2S+}) ionic molecule, \( R_{a} \) and \( R_{b} \) are the separations between the Xe and the two Na+ cores and \( \gamma \) is the angle between \( R \) and the Na_{2n}(X^{2S+}) internuclear axis.

3. Results and discussion

The structure and stability of the Na_{2n}(X^{2S+})Xe_{m} (n = 1–6) clusters are determined by fixing the internuclear distance of Na_{2n}(X^{2S+}) alkali dimer at its equilibrium distance of 6.83 a.u. determined by Berriche [18]. They are determined by using an accurate ab initio approach based on non-empirical pseudopotential, parameterized \( l \)-dependent polarization potential, and analytic potential forms for the Na+–Xe and Xe–Xe interactions. It is convenient to characterize the Na_{2n}(X^{2S+})Xe_{m} (n = 1–6) clusters by the couple of numbers \( (n,m) \) where \( n \) represent the number of xenon atoms and \( m \) is used to differentiate between the isomers of the same \( n \). In our previous works [16, 17] we studied the structure and stability of the small Li_{2n}(X^{2S+})Xe_{m} (n = 1–6) clusters. For the interaction between the Li_{2n}(X^{2S+}) alkali dimer in its ground state and the xenon atom, we observed that the Xe atom favored the external sites along the Li_{2n}(X^{2S+}) axis. This shows that the \( C_{nm}(12) \) isomer is more stable than the \( C_{nm}(11) \) isomer. In addition, we found for the Li_{2n}(X^{2S+})Xe_{m} clusters, that the most stable isomers are \( D_{nm}(21) \) for \( n = 2, C_{nm}(31) \) for \( n = 3, C_{nm}(41) \) for \( n = 4, D_{nm}(61) \) for \( n = 6 \). Based on our approach, the investigation of the alkali dimers in interaction with small clusters are extended in this paper by studying the structure and stability of Na_{2n}(X^{2S+})Xe_{m} (n = 1–6) by placing one, two, or more Xe atoms in different bonding sites. Actual calculations consist of extensive searches over a few dimensional internal coordinate spaces such that the symmetry of the structure is preserved.

3.1. Structure and spectroscopy of the Na_{2n}(X^{2S+})Xe

In this section, we investigate the structural and spectroscopic properties of the Na_{2n}(X^{2S+}) alkali dimer colliding with the xenon atom. This step represents the first step towards the study of the structure and stability of small Na_{2n}(X^{2S+})Xe_{m} clusters. The potential energy surfaces for the Na_{2n}(X^{2S+})Xe system are computed as
atom thus favors the positioning of the rare gas atom at one of the extremities of the Na$_2$(X$^2\Sigma_g^+$) alkali dimer molecule.

The spectroscopic constants corresponding to the equilibrium distance ($R_e$), the depth of the well ($D_e$), and the stretching frequency ($\omega_s$) of the potential energy surfaces corresponding to the six different angles ($\gamma = 0^\circ$, $11^\circ$, $25.3^\circ$, $39.7^\circ$, $68.5^\circ$, and $90.0^\circ$) are collected in Table 2. The analysis of these data shows that the equilibrium distance, the depth of the well, and the stretching frequency depend on the angle $\gamma$ showing the strong anisotropy of the Na$_2$(X$^2\Sigma_g^+$)-Xe system. In fact, we remark that the depth of the well and the stretching frequency decrease with increasing $\gamma$. The same behavior is observed for the equilibrium distance for the lowest four angles $\gamma$, then it increases for $\gamma = 68.5^\circ$ and $90.0^\circ$.

3.2. Structures and stabilities of small Na$_2$(X$^2\Sigma_g^+$)Xe$_n$ clusters

In this section, 15 structures of the Na$_2$(X$^2\Sigma_g^+$)Xe$_n$ ($n = 1$–6) clusters have been investigated: two for $n = 1$, 3, 5, and 6; three for $n = 4$; and four for 2. The potential energy surfaces for the 15 structures of the Na$_2$(X$^2\Sigma_g^+$)Xe$_n$ ($n = 1$–6) clusters with special different symmetry groups are computed by fixing the internuclear distance of Na$_2$(X$^2\Sigma_g^+$) ionic molecule at its equilibrium distance of 6.83 a.u. determined by Berriche [18]. These potential energy surfaces are presented in Fig. 3. In Fig. 4, we present schematic drawings of these 15 structures. In Table 3 we report the symmetry groups, the classical energy ($D_e$), the equilibrium distance ($R_e$), and the stretching frequency ($\omega_s$) of all studied isomers.

For $n = 1$, we studied two different structures having C$_{2v}$(11) and C$_{2v}$(22) symmetries. We remark that the potential energy surfaces of these structures tend to the same asymptotic limit. This limit, which equals ~0.224 689 a.u., is the energy of the Na$_2$(X$^2\Sigma_g^+$) at its equilibrium distance ($R_e = 6.83$ a.u.). In addition, the potential energy surfaces are attractive for the C$_{2v}$ and C$_{2v}$ structures and they present well depths of 942 and 65 cm$^{-1}$ located at 9.79 and 10.97 a.u., respectively. This shows that the linear isomer with C$_{2v}$(11) symmetry is much more stable than the structure with C$_{2v}$(12) symmetry where the Xe atom is placed perpendicular to the molecular axis of the dimer Na$_2$(X$^2\Sigma_g^+$). Indeed the well depth of the C$_{2v}$(11) isomer, which is equal 942 cm$^{-1}$, represents 43% of the Na$^+$-Xe interaction energy, which constitutes an equilibrium between the electronic and ionic energies.

For $n = 2$, four different structures are identified. Their symmetry groups are D$_{2h}$(21), C$_{2v}$(22), C$_{2v}$(23), and D$_{2h}$(24). The potential energy surfaces of these isomers and their schematic drawings are presented in Figs. 3 and 4, respectively. These potential energy surfaces are calculated as a function of the distance $R$ between the center-of-mass of Na$_2$ and each Xe atom for D$_{2h}$(21) and D$_{2h}$(24) isomers. It represents the distance between the center-of-mass of the Na$_2$ and the center-of-mass of Xe$_2$ cluster for C$_{2v}$(22) and C$_{2v}$(23) structures. We remark that at infinite distance the potential energy surfaces of D$_{2h}$(21) and D$_{2h}$(24) isomers dissociate into Na$_2$(X$^2\Sigma_g^+$) + 2Xe and tend to ~0.224 693 a.u. and those of C$_{2v}$(22) and C$_{2v}$(23) isomers dissociate into Na$_2$(X$^2\Sigma_g^+$) + Xe$_2$ and tend to

![Fig. 2. Orientational features of the rigid-rotor potential energy surfaces for six different angles: $\gamma = 0^\circ$, $11^\circ$, $25.3^\circ$, $39.7^\circ$, $68.5^\circ$, and $90.0^\circ$.](image-url)}
–0.225 574 a.u. In addition, the data reported in Fig. 3 and Table 3 show that the association energy of these isomers decreases in this order: \(D_{\infty h}(21)\), \(C_{2}(22)\), \(C_{2v}(23)\), and \(D_{2h}(24)\) with well depths of 1835, 1688, 493, and 133 cm\(^{-1}\) located at 9.83, 8.42, 7.21, and 10.51 a.u., respectively. Energetically, we find that the most stable isomers are the linear \(D_{\infty h}(21)\) and \(C_{2v}(23)\) isomers. We remark that the xenon dimer atoms are in the plane containing the \(Na_{2}(X^{2}S_{g})\) molecular system. Therefore, the \(Na^{+}(X^{2}S_{g})Xe\) cluster is more stable when the xenon atoms are placed at the two ends of the \(Na_{2}(X^{2}S_{g})\) ionic molecule. When we increase the number of Xe atoms from \(n = 3\) to \(6\) the most stable structures can be formed by appropriate combinations of substructures, such as linear as in \(C_{\infty v}(11)\), extended linear as in \(D_{\infty h}(21)\), and triangular shaped as in \(C_{2}(22)\). Two different structures, with the symmetry groups \(C_{2v}(31)\) and \(C_{3v}(32)\), have been studied for \(Na^{+}(X^{2}S_{g})Xe\) cluster. For \(C_{2v}(31)\) isomer, \(R\) represents the distance from the center-of-mass of \(Na_{2}\) to the center-of-mass of \(Xe\) cluster, while for \(C_{3v}(32)\) isomer, we have fixed one Xe atom at ~854 a.u. and we varied the distance between the center-of-mass of \(Na_{2}\) and the center-of-mass of \(Xe\) cluster. The potential energy surfaces of \(C_{2v}(31)\) and \(C_{3v}(32)\) isomers are attractive. We find the well depths of 3092 cm\(^{-1}\) for the \(C_{2v}(31)\) isomer and 2480 cm\(^{-1}\) for the \(C_{3v}(32)\) structure located at 9.45 and 7.85 a.u., respectively. Consequently, the most stable isomer is \(C_{2v}(31)\), which is a combination of \(C_{\infty v}(11)\) at its equilibrium geometry and the \(Xe\) cluster. The second structure \(C_{3v}(32)\), which is a combination of three xenon atoms forming an equilateral triangle cluster (\(Xe\)) perpendicular to the axis of the \(Na^{+}(X^{2}S_{g})\) ionic molecule is less stable. In the case of \(n = 4\), we determined the potential energy surfaces of the \(D_{2h}(41)\), \(C_{4v}(42)\), and \(C_{3v}(43)\) isomers. The well depths of these potential energy surfaces are 3138, 2843, and 1138 cm\(^{-1}\), respectively, located at 8.53, 6.75, and 16.43 a.u., respectively. The most stable isomer, \(D_{2h}(41)\), which is composed of two \(Xe\) clusters placed at the extremities of the \(Na^{+}(X^{2}S_{g})\). The \(D_{h}(42)\) isomer is obtained by combining the square cluster (\(Xe\)) perpendicular at the extremity of the \(Na^{+}(X^{2}S_{g})\) is less stable. The \(C_{3v}(43)\) isomer, which is much less stable compared to the \(D_{2h}(41)\) and \(C_{4v}(42)\) isomers, and is a combination of the \(Na^{+}(X^{2}S_{g})\) and the pyramid...
cluster (Xe$_4$). For the Na$_2$(X$^2\Sigma_g^+$)Xe$_n$ (n = 1–6) clusters, the first isomer C$_{∞v}$(11) is collected by Xe$_2$ and Xe$_3$ clusters placed at the extremities of the Na$_2$(X$^2\Sigma_g^+$) while the second isomer C$_{2v}$(52) is obtained by combining the C$_{∞v}$(11) isomer at its equilibrium geometry and the square cluster (Xe$_4$). Energetically the C$_{∞v}$(51) isomer is more stable than the C$_{2v}$(52) isomer. The well depths of their potential energy surfaces are 4221 and 2572 cm$^{-1}$ located at 8.15 and 6.92 a.u., respectively.

For n = 6, two different structures were investigated. The first isomer D$_{3h}$(61) is obtained by combining three Xe atoms (Xe$_3$) at each extremity of the Na$_2$(X$^2\Sigma_g^+$) ionic molecule. For this isomer, the centers of mass of Na$_2$ and Xe$_3$ are separated by a distance R. The second isomer D$_{2h}$(62) is obtained by combining D$_{3h}$(41) at its equilibrium geometry and two Xe atoms on the top of each extremity. Energetically, we find that the first isomer D$_{3h}$(61) is more stable with a well depth of 4558 cm$^{-1}$ located at 8.03 a.u.

### 4. Conclusion

In this paper, we have performed an accurate ab initio investigation for the potential energy surfaces describing the interaction between the Na$_2$(X$^2\Sigma_g^+$) alkali dimer and the Xe clusters of small variable size. We have used an accurate ab initio approach based on non-empirical pseudopotential, parametrized l-dependent polarization potential, and an analytic potential form for the Na–Xe cluster (Xe$_n$). For the Na$_2$(X$^2\Sigma_g^+$)Xe$_n$ clusters, the first isomer C$_{∞v}$(51) is collected by Xe$_2$ and Xe$_3$ clusters placed at the extremities of the Na$_2$(X$^2\Sigma_g^+$) while the second isomer C$_{2v}$(52) is obtained by combining the C$_{∞v}$(11) isomer at its equilibrium geometry and the square cluster (Xe$_4$). Energetically the C$_{∞v}$(51) isomer is more stable than the C$_{2v}$(52) isomer. The well depths of their potential energy surfaces are 4221 and 2572 cm$^{-1}$ located at 8.15 and 6.92 a.u., respectively.

### Table 3. Symmetry groups, classical energies ($D_e$), equilibrium distance ($R_e$), and stretching frequencies ($\omega_e$), of all isomers.

<table>
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<th>n</th>
<th>Symmetry</th>
<th>$D_e$ (cm$^{-1}$)</th>
<th>$R_e$ (a.u.)</th>
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and Xe–Xe interactions. The pseudopotential technique reduced the active number of electrons of Na$_2$(X$^2$Σ$_u^+$)Xe$_n$ (n = 1–6) clusters to only the Na valence electron. The core–core interaction for Na$^+$–Xe is included using accurate simple and double excitation (T) potential fitted using the analytical form of Tang and Toennies for a better description at intermediate distances. For the Xe–Xe potential interaction, we have used the analytical form of Lennard–Jones (LJ6–12). The potential energy surfaces for the interactions between the Na$_2$(X$^2$Σ$_u^+$) alkali dimer and the Xe$_n$ (n = 1–6) clusters were calculated for a fixed distance of the Na$_2$(X$^2$Σ$_u^+$) in its equilibrium distance. For n = 1, the potential energy surfaces were computed for an extensive range of the remaining two Jacobi coordinates, R and γ. It seems that the deepest well is associated with γ = 0°. We assume that the Xe atom would be attached at the extremity of the Na$_2$(X$^2$Σ$_u^+$) alkali dimer. In addition, we have investigated the structures of 15 isomers of the Na$_2$(X$^2$Σ$_u^+$)Xe$_n$ (n = 1–6) clusters: two isomers for n = 1, 3, 5, and 6; three isomers for n = 4; and four isomers for n = 4. Their potential energy surfaces are used to extract information on their stability. We find that the most stable isomers are C$_{∞v}$(11), D$_{∞h}$(21), C$_{2v}$(31), D$_{2h}$(41), C$_{3v}$(51), and D$_{3h}$(41).

References