Theoretical study of cationic alkali dimers interacting with He: $\text{Li}_2^+ - \text{He}$ and $\text{Na}_2^+ - \text{He}$ van der Waals complexes

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Abstract

We present a theoretical study on the potential energy surface and bound states of He-A_2^+ complexes, where A is one of the alkali Li or Na atoms. The intermolecular interactions were systematically investigated by high-level *ab initio* electronic structure computations, and the corresponding raw data were then employed to reproduce accurate analytical expressions of the potential surfaces. In turn, we used these potentials to evaluate bound configurations of the trimers from nuclear quantum calculations, and extract information on the effect of orientational anisotropy of the forces and the interplay between repulsive and attractive interaction within the potential surfaces. The spatial features of the bound states are analyzed and discussed in detail. We found that both systems are going under large amplitude stretching and bending motions with high zero-point energies. Despite the large differences in the potential well-depths, the correct treatment of nuclear quantum effects provides insights on the effect of different strength of the ionic interaction on the spectral structure of such cationic alkali van der Waals complexes, related with the mobility of ions and the formation of cold-molecules in He-controlled environments.

Introduction

Since the first experiments on doped ^4He droplets,¹⁻⁴ this field of research has attracted and fascinated both experimentalists and theorists.⁵⁻¹⁷ The interest of the scientific community is mainly due to the unique properties of the ultra-cold environment provided.¹⁸ Among of such properties one should mention that helium nanodroplets are remaining liquid even at zero temperature and are superfluid below the critical $T_\lambda=2.17$ K value with lack of internal friction allowing an almost free rotation of the molecular dopants inside,^{3,4,19,20} and their ability to quickly dissipate the excess energy of excited impurities.⁹ Further, due to the extremely low interaction energies, such He-doped impurities are also a great advantage for spectroscopy experiments. The He drops could act as an ideal matrix to achieve high

precision spectroscopic measurements, such as the development of the innovative HENDI (Helium Nanodroplet Isolation Spectroscopy) method for exploiting the very low temperature and low interaction with dopants for better spectral resolution.^{1,9} Within a variety of molecular dopants studied, alkali dimers have been the subject of several of them, *e.g.* HENDI experiments applied to Na₂, K₂ and Rb₂ dimers,^{12,21} with singlet or bound triplet molecules to reside on the surface of the droplet.

The solvation process of an impurity in He droplets depends on the dopant species and the nature of the underlying overall interaction with the surrounding He atoms. For neutral species, the He-alkali dimer interaction is even weaker than the He-He one, while the presence of charges on such impurities obviously modifies the interaction, with cationic alkali dimers to remain inside the droplet, as they interact more strongly with He atoms. Given the importance of such weak interactions in the microsolvation of such impurities in nano-sized He clusters, it is also a real challenge for theorists aiming for their accurate description. Moreover, this interest is increased due to the great development of photo-association spectroscopy of cold alkali atoms and their Bose Einstein condensations.²² Indeed, the formation of cold molecules by the method of photo-association requires a very good knowledge of the electronic properties of alkali dimers.

In this vein, a number of theoretical studies have been reported in the literature treating both neutral and charged alkali dimers in small He clusters.^{19,23–30} In particular, the microsolvation of neutral and cationic Li₂ in small He clusters^{23,24,26} has been investigated by employing *ab initio* interaction forces,²⁵ as well as potential energy surfaces for the heavier HeRb₂ and HeCs₂ in their triplet state of the dimers, following of quantum Monte Carlo simulations for studying the formation of high-spin alkali dimers in He clusters.^{27–29} However, a number of important questions remain about the alkali-doped helium clusters, as the properties of these systems may be investigated with different theoretical and experimental techniques.³¹ Recent high-resolution mass spectra for the lighter alkalis in He_{*n*} clusters, formed by electron ionization of doped He droplets display distinct anomalies in the ion

stability indicating that the number of atoms predicted in the first solvation shell is overestimated by theory.³¹

Thus, the aim of the present work is a theoretical investigation of two van der Waals(vdW) complexes, He-A_2^+ ($\text{A} = \text{Li}$ and Na), formed by the lighter cationic alkali molecules interacting with a He atom. These systems have been previously studied²⁵ by post Hartree-Fock methods at MP2 and MP4 levels of theory, and interaction potentials have been reported. In the light of new data on the stability of these ion clusters,³¹ we revised here their potential energy surfaces (PESs) employing *ab initio* CCSD(T) and MRCI(+Q) levels of theory and large basis sets in the electronic structure calculations, considering the extrapolation of the interaction energies at their complete basis set (CBS) limit. Further, we used a general interpolation scheme to generate the PESs, based on the reproducing kernel Hilbert Space (RKHS), and the inverse problem theory proposed by Ho and Rabitz.³² The potential and spectroscopy of these systems are determined and comparisons with previous results is provided.

The article is organized as follows: Section 2 outlines the computational methods and details, such as basis sets and extrapolation schemes used to calculate the interaction energies of the He-Li_2^+ and He-Na_2^+ systems, as well as comparisons of different methods employed here and in previous reported studies. The results of the overall potential representation, and the vibrational bound states calculations of the He-A_2^+ ($\text{A} = \text{Li}$ and Na) systems are presented and discussed in Section 3, while Section 4 summarizes some concluding remarks.

Methods and Computational Details

All *ab initio* electronic structure computations were carried out using Molpro program.³³ We used the Jacobi coordinates (r, R, θ) , with r being the Li_2^+ and Na_2^+ bondlengths, kept fixed at their corresponding r_e values in these calculations, while R is the intermolecular distance of the He atom from the center of the dimer, and θ the angle between the $\mathbf{r}$ and $\mathbf{R}$ vectors. We employed different levels of theory, such as the second order Möller-Plesset perturbation

(MP2), spin-restricted single and double excitation coupled cluster with perturbative triples (RCCSD(T)), as well as the multireference configuration interaction including Davidson correction (MRCI+Q) methods, to compute interaction energies of the complexes at various geometries. For all configurations studied the basis set superposition error (BSSE) was corrected by the counterpoise method.³⁴

As a first step, we calculated the interaction potential for the Li_2^+ and Na_2^+ dimers in their ground state ($X\ ^2\Sigma_g^+$) by selecting the cc-pV5Z (V5Z) and aug-cc-pV(Q/5)Z (AVQZ/AV5Z) basis sets at the RCCSD(T) and MRCI+Q levels of theory. The computed spectroscopic constants (r_e and D_e) are listed in Table 1, together with the available experimental^{35–38} and previous theoretical^{39–43} values. One can see that our results are in close accord with both theoretical and experimental data available. We should note that for Li_2^+ ion both r_e and D_e values are found to be sensitive to the level of theory used, while for the Na_2^+ only differences in the well-depths, of about 70 cm^{-1} , were obtained from the present RCCSD(T) and MRCI+Q calculations. Given the small differences found also with the experimental reported spectroscopic values, and for comparison reasons with previous theoretical calculations,²⁵ we have chosen to keep fixed the r_e bondlengths at 3.11 and 3.70 Å for the Li_2^+ and Na_2^+ dimers, respectively.

Table 1: Equilibrium distances (r_e) and the well-depths (D_e) for the Li_2^+ and Na_2^+ ionic dimers from the indicated level of theory or experiment.

	$\text{Li}_2^+ / \text{Na}_2^+$	
Methods/Basis set	$r_e(\text{\AA})$	$D_e(\text{cm}^{-1})$
RCCSD(T)/AVQZ	3.12 / 3.70	10341 / 7848
RCCSD(T)/V5Z	3.12 / 3.70	10344 / 7871
RCCSD(T)/AV5Z	3.12 / 3.70	10345 / 7872
MRCI+Q/AVQZ	3.15 / 3.70	10295 / 7804
MRCI+Q/V5Z	3.15 / 3.70	10296 / 7801
MRCI+Q/AV5Z	3.15 / 3.70	10297 / 7802
Theory [Ref. ³⁹] / [Ref. ⁴³]	3.127 / 3.61	10324 / 7872
Theory [Ref. ²⁵]	3.11 / 3.70	- / -
Expt.[Ref. ³⁵] / [Ref. ³⁸]	- / 3.60	10280 / 7975
Expt.[Ref. ^{36,37}] / [Ref. ⁴²]	3.110 / 3.60	10464 / 7730

For all He, Li and Na atoms, we used the AVTZ, AVQZ and AV5Z basis sets.^{44–46} Different basis sets were employed to extrapolate the computed energies at their CBS limit. In the present study, we explored the extrapolation of the energies by a three- and two-point schemes. The mixed Gaussian/exponential form,⁴⁷ $E_n = E_{CBS} + A e^{-(n-1)} + B e^{-(n-1)^2}$, where $n=3, 4$ and 5 corresponds to AVTZ, AVQZ and AV5Z basis sets, respectively, and the two-parameter expression⁴⁸ applied to the correlation energies given by $E_n = E_{CBS} + A/n^3$, using the energies from the AVQZ and AV5Z basis set calculations.

Table 2: Interaction energies for the He-Li₂⁺ and He-Na₂⁺ clusters at their linear configurations using the indicated basis sets and level of theory. ^a Comparison with theoretical values from previous studies²⁵ is also presented.

Methods	Basis set	ΔE (cm ⁻¹)	
		He-Li ₂ ⁺	He-Na ₂ ⁺
MP2 ^a	6-31G(3df)	-	-96
MP4(SDTQ) ^a	V5Z	-380	-
MP2	AVQZ/AV5Z	-324.33/-325.86	-88.89/-89.81
RCCSD(T)	AVTZ/AVQZ/AV5Z	-325.41/-339.88/ -341.13	-92.38/-97.46/ -98.21
RCCSD(T)	CBS(TQ5)	-341.81	-98.63
RCCSD(T)	CBS(Q5)	-342.41	-98.99
MRCI+Q	AVQZ/AV5Z	-340.55/-341.78	-98.10/-98.84
FCI	AVQZ	-342.16	-97.83

In Table 2, we list the calculated interaction energies of the two vdW complexes at their linear geometries ($\theta = 0^\circ$) from MP2, RCCSD(T), MRCI+Q, as well as FCI levels of theory. From the MP2/aug-cc-pVQZ/aug-cc-pV5Z calculations we found their interaction energies to be -324.33/-325.86 cm⁻¹ and -88.89/-89.81 cm⁻¹ for the He-Li₂⁺ and He-Na₂⁺, respectively, while from the RCCSD(T) using AVTZ/AVQZ/AV5Z basis sets, we compute their CBS[TQ5] and CBS[Q5] energies at optimized configurations to be -341.81/-342.41 cm⁻¹ and -98.63/-98.99 cm⁻¹ for the He-Li₂⁺ and He-Na₂⁺ systems, respectively. We should note that the obtained RCCSD(T)/CBS[Q5] values are lower than those from the RCCSD(T)/CBS[TQ5] estimates. Also we should point out the interactions of the alkali dimers with the He atom become significantly less attractive from Li₂⁺ to Na₂⁺ by about 250 cm⁻¹. In turn, the MRCI+Q/AVQZ/AV5Z results predicted -340.55/-341.78 cm⁻¹ and

-98.10/-98.84 cm^{-1} for each cluster, while the FCI/AVQZ energies were at -342.16 and -97.83 cm^{-1} , respectively. One can see that potential well-depths are deeper when moving from MP2 to FCI calculations using the same basis set, with lower energy from the MRCI+Q/AV5Z calculation than the RCCSD(T)/AV5Z, although no less than those from the RCCSD(T)/CBS[TQ5/Q5] ones. By comparing our present results with energies previously reported²⁵ from MP4(SDTQ)/V5Z and MP2/6-31G(3df) calculations for He-Li_2^+ and He-Na_2^+ , respectively, we found that the energies of those computations are considerably lower than all present calculations for the He-Li_2^+ systems, even when smaller basis sets have been used. In particular, differences of around 40 cm^{-1} are obtained between the MP4(SDTQ)/V5Z and RCCSD(T)/CBS[Q5], MRCI+Q/AV5Z or FCI/AVQZ energies for the He-Li_2^+ , while difference of almost 3 cm^{-1} were found between the previously reported MP2/6-31G(3df) and the present RCCSD(T)/CBS[Q5], MRCI+Q/AV5Z or FCI/AVQZ data for the He-Na_2^+ complex.

Figure 1: Minimum energy values obtained from MP2, RCCSD(T) and MRCI+Q methods for He-Li_2^+ and He-Na_2^+ complexes as a function of θ .

Figure 1, shows the interaction energy values along the minimum energy path as a func-

tion of angle θ at MP2, RCCSD(T)/CBS[Q5] and MRCI+Q levels of theory using the indicated basis sets. One can see in Fig. 1 that for both He-Li₂⁺ and He-Na₂⁺ clusters, and for all angular orientations the interaction energies from the RCCSD(T)/CBS[Q5] computations are very close to those from the MRCI+Q/AV5Z ones, and lower than those from the MP2/AV5Z energies by 16.6 and 9.2 cm⁻¹ for the linear wells and 3.5 and 2.6 cm⁻¹ at the T-shaped barriers for the He-Li₂⁺ and He-Na₂⁺, respectively. Therefore, we choose to consider the RCCSD(T)/CBS[Q5] energies as the reference data for both complexes hereafter in the present study.

Results and Discussion

The RCCSD(T)/CBS[Q5] interaction energies for the He-Li₂⁺ and He-Na₂⁺ were computed at a large and dense grid of the intermolecular R distances ranging from 2.5 Å and 3.5 Å, respectively, to 20 Å, for θ angles between 0–90° incremented by a step of 10°. The potential energy surface for the He-Li₂⁺ and He-Na₂⁺ complexes was constructed by using a general interpolation scheme based on the RKHS method proposed by Ho and Rabitz.³² Briefly, the 2D potential form is given by:

$$V(R, \theta; r_e) = \sum_{i=1}^{N_R} \sum_{k=1}^{N_\theta} V_{ik} q_1^{n,m}(x_i, x) q_2(y_k, y) \quad (1)$$

with $q_1^{n,m}$ and q_2 being the one-dimensional reproducing kernel functions for the distance-like, R , and angle-like, θ , variables,³² respectively. In the above equation, the reduced coordinates are $x = R$ and $y = \cos \theta$, N_R and N_θ are the number of *ab initio* calculated points in each coordinate, while

$$q_1^{n,m}(x, x') = n^2 x_{>}^{-(m+1)} B(m+1, n) {}_2F_1(-n+1, m+1; n+m+1; \frac{x_{<}}{x_{>}}) \quad (2)$$

where, $x_{>}$ and $x_{<}$ are the larger and smaller of the x and x' , respectively, and

$$q_2(y, y') = \sum_u \frac{(2l+1)}{2} P_u(y) P_u(y') \quad (3).$$

The n and m superscripts refer to the order of smoothness of the function and its asymptotic behavior at large distances, with $n = 2$, and $m=3$ with the R^{-4} accounts for the leading dispersion interaction between the He atom and A_2^+ molecular ion. B is the beta function, ${}_2F_1$ is the Gauss hyper-geometric function,³² and P_l the Legendre polynomials with $l=2k$, with $k=0-6$. The V_{ik} coefficients are obtained by solving Eq. (1), with $V(R_i, \theta_k; r_e)$ being the *ab initio* RCCSD(T)/CBS[Q5] energy at each (R_i, θ_k, r_e) grid point.

Figure 2: Comparison of the RCCSD(T)/CBS[Q5] interaction energies and the RKHS potential values as a function of R for He- Li_2^+ and He- Na_2^+ complexes for all angular orientations considered in the RKHS scheme.

Figure 2 shows a comparison for the RKHS potential curves and the *ab initio* RCCSD(T)/CBS[Q5] interaction energies as a function of R coordinate for each θ angle. For both clusters the linear configurations were found to be the global minimum on the PESs. For the He- Li_2^+ system the linear well was located at $R = 3.54 \text{ \AA}$ with a well-depth equal to 343.44 cm^{-1} for the RKHS potential compared to 342.55 cm^{-1} at $R = 3.53 \text{ \AA}$ obtained from the RCCSD(T)/CBS[Q5] calculations, while the T-shaped configuration at $R = 4.47 \text{ \AA}$ has energy of -16.86 and for

$R=4.46 \text{ \AA}$ at -16.85 cm^{-1} from the RKHS potential and RCCSD(T)/CBS[Q5] data, respectively. For the He-Na_2^+ the linear minimum of both the RKHS PES and RCCSD(T)/CBS[Q5] computations was found at $R = 4.49 \text{ \AA}$ and energy of -99.18 and -98.95 cm^{-1} , respectively, while the T-shaped configuration with $R = 4.94 \text{ \AA}$ is at energies of -11.41 and -11.42 cm^{-1} for the RKHS and RCCSD(T)/CBS[Q5] potential, respectively. Also we should mention that previous reported PESs for these complexes, fitted to MP4/V5Z and MP2/6-31G(3df) data, have estimated the potential minima and barrier heights at energies of about -380 and -12.5 cm^{-1} , and -96 and -6 cm^{-1} , for the He-Li_2^+ and He-Na_2^+ , respectively. As we mentioned above, such, mainly quantitative, differences are due to the level of theory and basis sets employed in the electronic structure calculations, that then have been used in the parameterization of the corresponding surfaces.

Figure 3: Minimum energy paths for the RKHS potentials of the He-Li_2^+ and He-Na_2^+ complexes together with the corresponding computed RCCSD(T)/CBS[Q5] interaction energies as a function of θ .

In Figure 3, we present the minimum energy path along all θ values of both vdW complexes from the RKHS PESs, together with the corresponding energies from the RCCSD(T)/CBS[Q5] calculations. From the linear geometries, $\text{He}\dots(\text{Li-Li})^+$ and $\text{He}\dots(\text{Na-Na})^+$, to the T-shaped configurations, $\text{He}\perp(\text{Li-Li})^+$ and $\text{He}\perp(\text{Na-Na})^+$ the potential values increase, with the inter-

action becoming less repulsive for larger angle values for both complexes. Again one should note the marked differences between relative energies of minima and barriers in the He-Li_2^+ and He-Na_2^+ complexes. In both case the RKHS PES describes smoothly the *ab initio* data for all angular orientations of the vdW clusters, and as one goes from He-Li_2^+ to He-Na_2^+ the repulsive effects decrease their importance with respect the attractive interaction forces, with the large changes occurring at angles between 20 and 50 °, especially pronounced in the He-Li_2^+ case (see in Fig. 3). In other words, the repulsion arising when the He atom approaches the nuclear center of the dimer ions are very similar in both Li_2^+ and Na_2^+ cases, while the attractive interactions are markedly different when the He atom approaches the one end of the alkali dimer ion. Their strength is highly dependent on the alkali atom, leading to the marked differences in terms of relative barrier heights and minima energies.

Figure 4: Two-dimensional contour plot of the analytical potential using the RKHS method of He-Li_2^+ (left panel) and He-Na_2^+ (right panel) complexes in the (θ, R) -plane.

In Figure 4, we show two-dimensional contour plots of the RKHS potentials for He-Li_2^+ and He-Na_2^+ complexes in the (θ, R) -plane with $r_e=3.11$ and 3.70 Å, respectively. One can see the two symmetric minima of the potentials, that correspond to linear with a well-depth of 343.44 cm^{-1} at $R = 3.54$ Å and 99.18 cm^{-1} at $R = 4.49$ Å for the He-Li_2^+ and He-Na_2^+ , respectively. The equipotential curves are at energies of $-342.8, -333.3, -294.6, -216.4, -103.5, -45.9, -29.0, -21.5, -17.9, -16.8 \text{ cm}^{-1}$ for the He-Li_2^+ plot, and $-99.1, -94.7, -81.6, -60.2, -38.3, -25.2, -18.0, -14.1, -12.0, -11.4 \text{ cm}^{-1}$ for the He-Na_2^+ system.

In turn, using the RKHS potentials, we perform variational quantum bound-state calculations considering zero total angular momentum ($J=0$). The Hamiltonian in Jacobi coordinates is given by, $\hat{H} = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R^2} + \frac{\hat{j}^2}{2\mu_2 r_e^2} + \frac{\hat{l}^2}{2\mu_1 R^2} + V(R, \theta; r_e)$, with the reduced masses being $\frac{1}{\mu_1} = \frac{1}{m_{He}} + \frac{1}{2m_{A_2^+}}$ and $\frac{1}{\mu_2} = \frac{1}{m_A} + \frac{1}{m_A}$, where m_{He} , m_{Li} and m_{Na} are the atomic masses of 4He , 7Li and ${}^{23}Na$ isotopes.⁴⁹ $\hat{j}$ and $\hat{l}$ are the angular momentum operators associated with the vectors $\mathbf{r}$ and $\mathbf{R}$, respectively, leading to a total angular momentum $\hat{J} = \hat{l} + \hat{j}$.

The Hamiltonian is represented on a finite two-dimensional grid in R and θ coordinates, and keeping $r = r_e$ at 3.11 Å and 3.70 Å for $He-Li_2^+$ and $He-Na_2^+$ complexes respectively. For the angular coordinate we used orthonormalized Legendre polynomials $P_j(\cos\theta)$ as basis functions, with up to 48 and 49 values of the diatomic rotation j , for even and odd symmetry, respectively, while in R coordinate, we employed up to 160 and 150 DVR (discrete variable representation) particle-in-box functions⁵⁰ over the range from $R=2.5$ and 3.5 to 20 Å for the $He-Li_2^+$ and $He-Na_2^+$, respectively. By diagonalizing the corresponding hamiltonian matrix, we obtained the energy eigenvalues and eigenfunctions for each system. A convergence of 10^{-4} cm^{-1} was achieved in the present bound state calculations.

Table 3: Vibrational energies (in cm^{-1}) of all bound states ($J=0$) of $He-Li_2^+$ and $He-Na_2^+$ systems.

n	He-Li ₂ ⁺	He-Na ₂ ⁺
	j = even / odd	
0	-226.9973 / -226.9973	-56.8136 / -56.8136
1	-154.3356 / -153.3356	-35.1185 / -35.1185
2	-109.9738 / -109.9738	-21.5786 / -21.5786
3	-79.2128 / -79.2128	-16.7661 / -16.7637
4	-57.0517 / -57.0517	-8.8926 / -8.8660
5	-42.9834 / -42.9834	-7.1111 / -6.3330
6	-19.8159 / -19.6038	-5.0730 / -5.0727
7	-12.7404 / -12.7185	-2.8347 / -1.3485
8	-9.5563 / -9.5484	-1.6370 / -0.2082
9	-7.1269 / -2.7935	-0.3053 /
10	-2.8130 / -2.1227	
11	-2.1682 / -0.6748	
12	-0.0748 /	

In Table 3 we list all bound vibrational states up to $He + A_2^+$ dissociation limit of the

RKHS PESs: in total 25 for the He-Li_2^+ , and 19 for the He-Na_2^+ . The parity of the total wavefunction with respect to the exchange of two identical atoms has been included, so depending of the parity of the j quantum numbers we obtained even or odd vibrational states. The ground vibrational states were found at energies of -227.00 and -56.81 cm^{-1} , with the corresponding zero-point energy (ZPE) values of 116.44 and 42.37 cm^{-1} , counting 34% and 43% of the potential well-depths, for the He-Li_2^+ and He-Na_2^+ , respectively. In Table 3 one can also see that some of the lowest-lying, even and odd, vibrational states for the He-Li_2^+ ($n=0-5$) and He-Na_2^+ ($n=0-2$), are double degenerated, and correspond to energies below the potential barrier, while the remaining higher-lying even and odd parity states are found at different energies. Such spectral structures are related to the potential barrier at the T-shaped configurations that connects the two symmetric linear minima of the PESs. Thus, below the potential barrier the states have a doublet structure, while once the energy of the states overcomes it the states show different behavior depending on their parity.

By comparing with previous available data²⁵ we found significant quantitative differences in all bound states calculated for both complexes, that are mainly arised from the underlying PESs employed. As we mentioned above, potential well-depths and corresponding barriers' heights were found at different energies, so the previous study²⁵ predicts a more stable linear He-Li_2^+ complex by near 30 cm^{-1} , and a less stable He-Na_2^+ linear conformer by 7 cm^{-1} . For the He-Li_2^+ cluster in accord with the present results the potential supports, apart of the ground state, another 12 even and 11 odd parity states up to its dissociation, while for the He-Na_2^+ system the previous MP2-based PES²⁵ predicts in total 16 (including the vibrational ground state) bound levels, instead of 19 (10 even and 9 odd) states up to the corresponding dissociation limit.

In Figure 5, we show the radial and the angular distributions for all bound states (even and odd symmetry) calculated for He-Li_2^+ and He-Na_2^+ . We discuss the results presented in the plot as follows. One can see first that the low-lying bound states (at energies well

Figure 5: Radial (left) and angular (right) distributions for all bound states of He-Li_2^+ (grey) and He-Na_2^+ (blue) for both even (e) and odd (o) (see solid and dashed lines, respectively) vdW states.

below the corresponding potential barrier), such as the $n=0-5$ states for the He-Li_2^+ complex and $n=0-2$ for He-Na_2^+ , show a strong localization of the He atom in the linear potential wells, and one could assign them to stretching and bending vibrational modes. For both complexes, the ground $n=0$ state is nodeless localized in the two equivalent linear wells, as one can see in their angular distributions, while the radial density distribution of the He-Na_2^+ is localized at larger R values compared to those of He-Li_2^+ , around 4.6 and 3.6 Å, respectively, indicating the weakness of the interaction of the heavier alkali molecules with He atom. The next $n=1$ and 3 states describe bending motions of He atom, as they show nodes in their angular distributions, while the $n=2$ state of both He-Li_2^+ and He-Na_2^+ , the $n=5$ one for the He-Li_2^+ and the $n=6$ for the He-Na_2^+ , correspond to excited stretching motions with clear radial nodes in the corresponding distributions. In turn, the bound states with energies nearby (just below and/or above it) the potential barrier, like the $n=6-8$ and $n=3-5$ for He-Li_2^+ and He-Na_2^+ , respectively, both radial and angular distributions are moving to larger R distances and configurations with some population at the region of the T-shaped barrier, corresponding to mixed stretch-bending motions. Also, as we mentioned above, we should note that the differences in the PESs' shape between the two complexes, especially at the region close to the potential barrier clearly affect the spatial behavior of these states, depending on the nuclear rotational symmetry, and thus marked differences observed. Finally, the high-lying bound states show a more complicated spatial structure with extended angular distributions, and clearly visible differences between even and odd states. We can see that the angular distributions of the odd states present an additional central node, with large bending excitation of the He atom, while even states show mainly T-shaped complexes even at larger dissociating distances.

Conclusions

In this paper, we present a theoretical study for the He–Li₂⁺ and He–Na₂⁺ vdW clusters focused on the interaction between the lighter alkali dimer cations and a He atom. On the theoretical side, accurate description of such intermolecular forces is still in a huge demand in studies related with mobility of ion impurities and collision dynamics in cold He-environment. To this end, we first carried out high level *ab initio* calculations, by carefully checking the performance of the level of theory, as well as the convergence of the basis sets employed. We found that previous studies overestimate or underestimate the well-depths and barrier heights of both complexes, given the difficulties associated with those calculations. Therefore, the interaction energies in the present study are obtained from CCSD(T) computations employing large basis sets, and then extrapolated at their CBS[Q5] limits. Using the general interpolation procedure with the RKHS method we generated *ab initio*-based RCCSD(T)/CBS[Q5] interaction potentials for these complexes, and vibrational quantum bound state calculations were then performed. We found that the collinear configuration with the He atom attached to the Li₂⁺ and Na₂⁺ ionic dimers, is the most stable conformer for both trimers, with dissociation energies of 227.00 and 56.81 cm^{−1}, respectively.

Such potential expressions presented here, could serve, within the sum-of-potential approach, to describe microsolvation processes of such cationic impurities in He nanodroplets. One expects that the competition between the dominant ionic forces in the case of Li₂⁺ and Na₂⁺ with respect to the He-He network of interactions will play a crucial role in structuring the shape of the larger clusters, and small differences in the energetics of the trimers could alter the stability of the observed structures of the larger species. Thus, accurate description of the trimers’ energetics could provide additional initial insights for controlling the stabilization of such systems, that could be tracked in their observation in the recent high-resolution mass spectra experiments, and identify the observed anomalies of specific finite-size He-doped alkali cations. In this vein, it is also interesting to perform quantum dynamic simulations for higher-order clusters⁵¹ to verify the zero-point effects to their dissociation energies. Work in

this direction is currently in progress.

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Graphical TOC Entry

Minimum energy curves and vibrational (even) bound energies of HeLi_2^+ and HeNa_2^+ clusters.