Ionic dimers in He droplets: Interaction potentials for $\text{Li}_2^+\text{-He}$, $\text{Na}_2^+\text{-He}$, and $\text{K}_2^+\text{-He}$ and stability of the smaller clusters

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Ionic dimers in He droplets: Interaction potentials for $\text{Li}_2^+ - \text{He}$, $\text{Na}_2^+ - \text{He}$, and $\text{K}_2^+ - \text{He}$ and stability of the smaller clusters

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We present post Hartree-Fock calculations of the potential energy surfaces (PESs) for the ground electronic states of the three alkali dimer ions Li_2^+ , Na_2^+ , and K_2^+ interacting with neutral helium. The calculations were carried out for the frozen molecular equilibrium geometries and for an extensive range of the remaining two Jacobi coordinates, R and θ , for which a total of about 1000 points is generated for each surface. The corresponding raw data were then fitted numerically to produce analytic expressions for the three PESs, which were in turn employed to evaluate the bound states of the three trimers for their $J=0$ configurations: The final spatial features of such bound states are also discussed in detail. The possible behavior of additional systems with more helium atoms surrounding the ionic dopants is gleaned from further calculations on the structural stability of aggregates with up to six He atoms. The validity of a sum-of-potential approximation to yield realistic total energies of the smaller cluster is briefly discussed *vis-a-vis* the results from many-body calculations. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172610]

I. INTRODUCTION

Clusters of variable size containing ^4He atoms as components constitute an important environment as a nonhomogeneous quantum system that is fairly different from similar examples provided by, say, a film on a solid surface or a macroscopic liquid with a free surface. The quantum nature of such an adaptive system is further highlighted when one or more dopant species are picked up by a given cluster and therefore the overall structuring of the finite-size "solvent" becomes perturbed by the presence of one or more "solute" species that markedly modify the nature of the overall interaction.¹⁻³

The nature of the perturbation and its consequences on the quantum structures which are formed by the insertion of the dopant species into the initial cluster have been the subject of many recent studies, since the analysis of helium clusters modified by the inclusion of neutral atomic and molecular species has become a burgeoning subject with a great deal of theoretical and experimental interests. This has happened precisely because of the intriguing interplay between weak interactions and quantum effects.^{1,4}

One of the main physical reasons for the different behaviors of the ^4He cryomatrices *vis-a-vis* the more usual solid matrix isolation techniques⁵ is related to the large quantum delocalization of the helium atoms within the droplet, so that

the solvent partners are able to adopt in the vicinity of the molecule a unique and markedly structured configuration that describes the lowest, and nodeless for ^4He , quantum state of the system. In other words, in contrast with the crystal-like behavior of the interactions within a solid matrix, the He cluster provides a tailored void that depends on the dopant species.¹

The presence of charges on the impurity obviously modifies the situation in the sense that closed shell, weakly bound anionic species such as H^- exhibit strongly repulsive interactions with the helium atoms and therefore are rapidly ejected by the cluster, largely residing on their surfaces,⁶ while cationic impurities are seen to interact much more strongly with the surrounding atoms and therefore get rapidly "solvated" inside the cluster thereby forming the so-called snowball structures.⁷

Recent theoretical studies on ionic alkali atoms⁸ have indeed analyzed the above behavior and their findings have also been confirmed by our own recent studies on ionic lithium atoms as dopants of ^4He clusters.⁹ We have further looked into the behavior of He clusters doped with neutral alkali atoms¹⁰ and dimers^{11,12} by analyzing the relevant interactions and the structures which originate from such potentials.

In the present work we intend to study the forces between ionic alkali molecules and one He atom by computing from *ab initio* quantum methods the relative potential energy surfaces (PESs), following our recent work¹³ on the changes

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of the interaction fields for the two situations of a neutral and ionic diatomic dopant, obtained from full *ab initio* calculations for Li_2 and Li_2^+ with one He atom. The data reported here for the Li_2^+ molecule have already been discussed in part there but will be repeated and extended here in comparison with other ionic species.

The work is organized as follows. The next section describes the detail of the computational method and the overall spatial shape of each PES for the three cationic alkali dimers, while Sec. III reports the calculations of the corresponding bound states when the complex is taken to be non-rotating in space ($J=0$). Section IV further reports a set of structure optimization calculations which uses *ab initio* forces in order to predict the structural properties of the smaller clusters containing up to six helium atoms.

II. THE POTENTIAL ENERGY SURFACES

The calculations were carried out at the post Hartree-Fock level employing the MP4(SDTQ) method with a cc-pV5Z basis set for Li_2^+-He system and at the MP2 level with a mixed basis for Na_2^+-He and K_2^+-He . For the last two systems the basis set was a cc-pV5Z on He and 6-31(3*df*) for the metals (see Sec. IV and the energies of Table III for a discussion about the choice of basis sets). As we said above, the dimer ion geometries were kept at their equilibrium values: For the Li_2^+ the chosen value of 3.11 Å was determined by optimizing the geometry in a separate calculation. The same procedure was then followed for Na_2^+ where the value of 3.7 Å was obtained. In the case of K_2^+ the bond distance was taken from the experiments¹⁴ and a value of 4.4 Å was used in the calculations. All *ab initio* energies have been basis set superposition error (BSSE) corrected using the counterpoise correction¹⁵ as implemented in GAUSSIAN 03.¹⁶ We have performed several tests in order to be sure that the drastic change in methodology moving from MP4 to MP2 calculations would not unduly affect our results. We therefore believe that the energetic trends in the cluster behavior that we are going to present below are not an artifact from the change of methodology. We have indeed tested on the Li_2^+He species the change in the energy of its minimum structure (see Fig. 11 and Table II); when moving from MP4 to MP2 with cc-pVQZ basis set, the energy changed from -369.12 to -351.67 cm^{-1} , while when using the cc-pV5Z basis set it changed from -377.77 to -359.78. Hence the energy changes due to the calculation scheme are comparable and are even less than those we obtain when changing the basis set. By repeating the same test for Na_2^+He minimum structure and using the mixed basis set, we see an energy change from -93.5 to -102.0 cm^{-1} : here again the change is comparable to what we obtain by changing the basis sets (see Table III).

In order to make the employment of the potential energy surfaces in further studies more manageable, we have decided to obtain a suitable analytical representation of the raw points using a nonlinear fitting procedure based on the minimization of the square deviation via the Levenberg-Marquadt method.¹⁷ As reported earlier¹³ we find particularly useful to follow the procedure outlined by Groenenboom and

FIG. 1. Coordinates used in the fitting formula.

Balakrishnan¹⁸ simplified by the fact that the internuclear dimer distance is held fixed. The full interaction can be written as

$$V_{\text{tot}} = V(R_a, \theta_a) + V(R_b, \theta_b) + V_{\text{LR}}(R, \theta), \quad (1)$$

where the coordinates are those reported in Fig. 1.

The first two contributions represent the anisotropic interactions at short range and are written in terms of Legendre polynomials

$$V(R_a, \theta_a) = \sum_{n=0}^{n_{\text{max}}} \sum_{l=0}^{l_{\text{max}}} R_a^n \exp(-\beta R_a) P_l(\cos \vartheta_a) C_{nl}^a, \quad (2)$$

where the symmetry of the homonuclear molecule $C_{nl}^a = C_{nl}^b$ is given. The long-range contribution is instead expressed in Jacobi coordinates and is given by

$$V_{\text{LR}}(R, \theta) = \sum_N \sum_{L=0}^{N-4} \frac{f_N(\beta R)}{R^N} P_L(\cos \vartheta) C_{NL}^{\text{LR}}, \quad (3)$$

where the f_N damping functions are those defined within the well-known Tang-Toennies potential model.¹⁹

For the Li_2^+-He system¹³ we have employed a representation given by $n_{\text{max}}=8$ and $l_{\text{max}}=4$ and two long-range anisotropic terms: C_4 and C_6 . The latter terms were employed in order to correctly represent the long-range multipolar expansion of a neutral, polarizable atom interacting with a pointlike charge:

$$V_{\text{LR}} = \frac{f_4(\beta R)}{R^4} [P_0(\cos \theta) C_{40}^{\text{LR}}] + f_6(\beta R) R^{-6} \times [P_0(\cos \theta) C_{60}^{\text{LR}} + P_2(\cos \theta) C_{62}^{\text{LR}}]. \quad (4)$$

The total number of 1135 points was reduced to 1065 by excluding the repulsive energies with values above 5000 cm^{-1} . The final standard deviation was 0.07 cm^{-1} . The same procedure was then used for Na_2^+ where we fitted 1119 points with a standard deviation of 0.07 cm^{-1} . Finally, in the case of K_2^+ all the 1020 points were employed and $n_{\text{max}}=6$ and $l_{\text{max}}=4$ were sufficient to get a standard deviation of 0.14 cm^{-1} . The (x, y) maps reported by Fig. 2 allow us to make a detailed comparison of the differences of behavior between the three ionic species examined in the present work.

All minimum structures are given by linear complexes with a potential barrier between the two $D_{\infty h}$ symmetry configurations. Furthermore, the repulsive walls are all very similar since they essentially describe the strong Coulombic repulsion arising when the He atom approaches the nuclear centers of the dimer ions, while the attractive regions show

FIG. 2. Computed potential maps for the three systems of the present study. From upper to lower panel we have Li_2^+ , Na_2^+ , and K_2^+ . All energy values are in cm^{-1} . The coordinates are $x=R \cos \theta$ and $y=R \sin \theta$ with all values in Å.

marked differences especially in terms of relative barrier heights and minima locations. To show this aspect, we additionally report in Fig. 3 the angular minimum energy paths which are obtained by joining the radial minima at different orientations.

It is interesting to keep in mind the differences in values given by the barriers to tunneling for the three title systems, since they will have a direct bearing on the structures that will be exhibited by the bound states of these systems and which will be described in the next section.

A different perception of the angular anisotropies which exist in the three complexes is presented by Fig. 4, where we show the potential energy profiles at two specific orientations: the one for $\theta=0^\circ$ corresponds to the collinear approach of the helium partner while the $\theta=90^\circ$ describes the approach along the midbond perpendicular path.

The data reported in the figure clearly show how the repulsive effects increase their importance with respect to the attractive long-range interaction forces as one goes from the $\text{Li}_2^+\text{-He}$ to the $\text{K}_2^+\text{-He}$ case. The collinear well depths, in fact, vary from about -380 cm^{-1} for $\text{Li}_2^+\text{-He}$ to about -96 cm^{-1} for $\text{Na}_2^+\text{-He}$ and to about -38 cm^{-1} for $\text{K}_2^+\text{-He}$, while the corresponding barrier heights move from about -12.5 cm^{-1} for lithium to -5 cm^{-1} for sodium and to -4 cm^{-1} for potassium dimer ions. Their locations from the molecular center of mass in each system also vary from 3.5 Å for $\text{Li}_2^+\text{-He}$ to 4.5 and 5.5 Å for sodium and potassium dimer ions as partners. In other words, we clearly see from the present calculations that the interactions of the three alkali dimers with one helium atom become increasingly less attractive and show larger repulsive cores when one moves from lithium to potassium.

FIG. 3. Computed angular minimum energy paths for the three complexes discussed in the main text.

III. THE BOUND STATES OF THE COMPLEXES

The full spectrum of the bound eigenstates of the three nonrotating complexes was obtained following two different procedures in order to provide an internal check on the quality of the present results. In the present systems we have neglected the spin-rotational constant of the diatomic molecule since it should be two orders of magnitude smaller than their rotational constants,^{20,21} and therefore we have neglected the splitting of the rotational levels that this coupling causes for the $^2\Sigma$ molecules of the present study. This means that the coupling scheme of the various angular momenta we have employed is the same as that of a $^1\Sigma$ molecule.²² As we have mentioned above, we are interested in the bound states of the nonrotating complexes and therefore we will consider

here only the case in which there is no rotation of the entire complex (the total rotational angular momentum is zero) while the total angular momentum is $\frac{1}{2}$ due to the additional presence of the molecular electronic spin.²² In the first instance, we have employed the BOUND code²³ program extending the radial integration from 3.0 to 30 Å, using a basis set made up of the rotational states of the dimer ions which were included in the coupled channels (CC) approach up to $j_{\max}=24$. We have also performed a discrete variable representation (DVR) calculation which followed the procedure we have recently given in detail.²⁴ Here we have used 400 radial grid points and Legendre polynomials up to order $j=24$ as in the BOUND calculations. In both cases the parity of the total wave function with respect to the exchange of the

FIG. 4. Computed angular "cuts" of the full potential energy surfaces of the three title systems.

TABLE I. Computed bound states for the $J=0$ complex structures of the three systems. All values are in cm^{-1} . See main text for further details.

Index	j even		j odd	
	BOUND	DVR	BOUND	DVR
Li_2^+-He				
0	-254.64	-254.64	-254.64	-254.64
1	-177.57	-177.57	-177.57	-177.57
2	-125.11	-125.11	-125.11	-125.11
3	-97.44	-97.44	-97.43	-97.44
4	-68.07	-68.06	-68.07	-68.06
5	-48.74	-48.74	-48.74	-48.74
6	-22.26	-22.26	-22.22	-22.22
7	-17.08	-17.08	-17.05	-17.05
8	-12.72	-12.72	-12.71	-12.71
9	-9.50	-9.50	-9.49	-9.49
10	-5.52	-5.52	-1.82	-1.82
11	-1.51	-1.51	-0.21	-0.21
12	-0.06	-0.05		
Na_2^+-He				
0	-49.56	-49.56	-49.56	-49.56
1	-26.23	-26.23	-26.23	-26.23
2	-15.67	-15.67	-15.67	-15.67
3	-8.97	-8.97	-8.96	-8.96
4	-3.68	-3.68	-3.65	-3.65
5	-2.97	-2.97	-1.82	-1.82
6	-1.60	-1.61	-1.56	-1.56
7	-0.34	-0.34	-0.02	-0.02
K_2^+-He				
0	-17.47	-17.47	-17.47	-17.47
1	-8.57	-8.57	-8.57	-8.57
2	-3.57	-3.57	-3.57	-3.57
3	-2.48	-2.48	-2.33	-2.33
4	-0.73	-0.73	-0.26	-0.26
5	-0.27	-0.27		

two identical atoms which make up the molecule has been explicitly included. The results are divided into two sets depending on the parity of the j quantum numbers and are reported in Table I, where we show, for the three systems, the findings obtained by using both computational approaches.

The following comments could be made from a perusal of the data in the table.

1. The numerical agreement between the eigenvalues produced via two different methods is really very satisfactory: All across the spectrum we have identical results to two decimal figures. The dissociation channel considered here is, obviously, the $X_2^++\text{He}$ breakup.
2. As expected, the number of bound states decreases when moving to the heavier alkalis and the corresponding zero-point energy (ZPE) values also markedly decrease along the series.
3. Since the states of the rotor basis set may be either even or odd with respect to the C_2 axis of the system, we have two different spectral series. For energy values well below the potential barrier at 90° , the energies of the two states are almost the same (the difference between the first two states is below 10^{-5} cm^{-1} for all the

three systems) and give rise to a doublet structure. Only when the energy of the bound state overcomes the barrier, the corresponding states of the complex exhibit marked differences of spatial behavior depending on the parity of the j quantum number of the rotational/angular basis.

In the potential cuts shown in Fig. 4 we have also drawn the relative locations, on the energy scale, of a few of the lower-lying bound states of the complexes. The same idea, but for the higher-lying states, is implemented by the panels of Fig. 5, where we additionally show (lower panels) the top areas of the barriers to the rotation of the helium atom.

We further report in the following figures the structure of the wave functions of the bound states of the Li_2^+-He system only since they are indicative of the behavior of all three complexes. In the upper panels of Fig. 6 we show the radial and angular distributions for the two selected states (of even symmetry) which lie below the 90° barrier. We clearly see that such states correspond to strongly localized He atoms in the collinear wells and with negligible population in the region of the barrier maxima. In the lower panels of the same figure we show the distributions for a state just below the barrier ($n=5$) and one ($n=9$) that lies well above it (see Fig. 5). The radial distributions clearly acquire a more complicated nodal structure and correspond to a stretching vibrational “mode” of the helium atom along the radial coordinate. The barrier effect is still well marked and the He partner remains largely localized along the linear structure. The situation becomes very different when we look at the highest bound states with energies above the angular barrier. The results of our calculations for such radial and angular distributions are shown by Fig. 7.

The effect of the nuclear rotational symmetry on the spatial shape of the bound states is clearly visible in the angular distributions, since we can now see the additional central node for the odd states. We thus see that, although their energy is located well above the 90° barrier, these high-lying odd states still describe the adatom as undergoing large bending motion but not getting localized in the 90° region of the PES. On the other hand, we see that the corresponding even configurations describe a T-shaped complex with the adatom chiefly localized within a sort of C_{2v} symmetry of a very floppy system. These marked differences between even and odd states may have some bearing in the structuring of fermionic helium clusters around the dopant molecule in the sense that the sequential allocation of additional ^3He atoms in the various energy levels may depend on either having an *ortho* or *para* impurity in the droplet. Another interesting difference in the internal dynamics, and one which could have some bearing on the relative stabilities of cluster growth, is further provided by the presence of rotational zero-point energies for the odd- j ground states as opposed to the even- j ones where $j=0$ value is allowed.

A qualitative classification of some of the bound states in terms of normal modes could be attempted for all three complexes: As an example of it we show results for the Li_2^+-He system in Fig. 8. We report there the contour maps of the wave functions for some selected (even- j) states. Negative

FIG. 5. Potential energy cuts along the $\theta=90^\circ$ Jacobi angle for the three systems of the present study (upper panels) and the higher energy regions of the corresponding angular minimum energy path curves (see Fig. 3) as a function of the θ values. Energy values are in cm^{-1} , distances are in $\text{\AA}$, and angles are in degrees.

and positive lobes of the wave function are distinguished by the different line style (dashed and solid). The thick solid line in the center of the plots represents a repulsive (1000 cm^{-1}) energy isoline of the PES and gives an idea of the “size” of the central molecular diatom (which has its internuclear axis vertically aligned in the figure plane). We report results for the j -even states, but entirely similar mapping could be obtained for the j -odd states (for $n=0, 1, 2, 4, 9$) whereby we have an additional nodal surface crossing the molecular axis (horizontally in the plots of Fig. 8) and thus we see a change of sign of the wave function lobes across this surface.

The ground state is clearly represented by a nodeless wave function localized in the two equivalent linear wells (the “twin” j -odd state is essentially equivalent but we have one additional nodal surface and the two lobes have different signs). The next state has an angular node and appears to

describe a “bending” type of motion of the helium atom. In the next state we clearly see a radial node and therefore we may argue that it is representing an excited “stretching” motion of the complex.

As one moves to the higher excited states, however, we find that, while the $n=4$ state can still be classified as corresponding to a mixed excitation (bending+stretching) mode, it becomes much harder to follow that qualitative picture for the higher bound states. As examples we show in Fig. 8 the $n=9$ and 10 states. We can see that the $n=9$ state, located above the inversion barrier, is still largely a stretching state, although nodes in that wave functions are also present across the bending motion. As we have seen before the $n=10$ state is instead moving away from the collinear geometries and clearly presents a wave function which now describes a floppy, T-shaped complex configuration.

FIG. 6. Computed radial (left) and angular (right) distributions for four different states of Li_2^+-He .

FIG. 7. Computed radial (left) and angular (right) distributions for the $n=10$ and $n=11$ bound states of Li_2^+-He . Both even (solid lines) and odd (dashes) states are shown in each panel.

A last bit of information on the present systems can be gleaned by looking at the results of Fig. 9, where we report the radial extension of the ground vibrational state for all three complexes analyzed in the present work: one clearly see for all of them a marked delocalization of the helium

atoms despite the decreasing strength of the ionic interactions along the series. Furthermore, we see that the “excluded volume” due to the impurity molecule increases markedly from Li_2^+ to K_2^+ since the distributions have maxima that move out from about 3.5 to about 5.7 Å. At the same

FIG. 8. Isodensity lines for the bound wave functions of the Li_2^+-He complex, reporting the lowest three bound states in the upper row of panels and some of the excited states in the lower row of panels. Only j -even states are reported. Distances are in Å.

FIG. 9. Computed radial density distributions for the ground states of the three complexes. Distances are in Å.

time, due to the greater weakness of the interaction when going from Li_2^+ to K_2^+ , the distributions indicate larger delocalizations of the He atom.

IV. STRUCTURAL STABILITY OF THE SMALLER CLUSTERS

We have further carried out a careful search of possible minimum energy structures by exploring directly the potential energy surfaces (PESs) of Li_2He_n^+ , Na_2He_n^+ , and K_2He_n^+ obtained from quantum, many-body calculations. Once a suitable minimum geometry was found, we additionally performed a frequency calculation in order to verify the nature of the localized point through the well known analysis of the Hessian eigenvalue properties. This procedure was selected for two reasons: First, the relative weakness of the He–He interactions compared to the M_2^+ –He ones results in very floppy potential functions where the round off errors in the Hessian accumulate rapidly and consequently a great number of iterations may be required to find the global minimum. In fact, for some of the present clusters we were not able to identify the global minimum through the Hessian analysis. The second and, perhaps, more important factor was to identify other local minima which energetically may be lying very close to the absolute one and hence be easily accessible to such highly delocalized quantum solvent.

The search of the minima along the many dimensional PESs starts with the simplest mono-He clusters Li_2He^+ , Na_2He^+ , and K_2He^+ using the interactions described in the previous sections. Our analysis of their structures reveals several interesting features: Even though the dissociation energies of the three molecules greatly differ among each other, the collinear approach of the helium atom is always the most favored one and it is much more probable than the C_{2v} approach. The scaled rotational potential energy as a function of the Jacobi angle θ is given in Fig. 10. The potential energy corresponding to the minimum R along each θ is linearly scaled as

FIG. 10. Scaled potential energies for $M_2\text{He}_n^+$ as a function of the (He–O–M) angle. The scaled potentials are dimensionless and their zeros represent the center of mass of the diatomic molecule.

$$V_s(\theta) = \frac{(V(\theta) - V(0^\circ))}{(V(0^\circ) - V(90^\circ))}. \quad (5)$$

We clearly see that the scaled behavior is very similar for Na_2^+ and K_2^+ , whereas for Li_2^+ a sharper increase is observed around 35° . It is, however, evident that the anisotropy of the interactions is still qualitatively similar for all three dimers, and we therefore expect that the structures of the He clusters formed around Li_2^+ , Na_2^+ , and K_2^+ should largely resemble each other.

On the other hand, the relative strength of the interactions (ranging from 40 to 350 cm^{-1}) indicates that the stability of these structures may be quite different since there is one further factor determining the structure and the stability of these van der Waals clusters, i.e., the size the alkali atoms. Thus, as we go from Li_2^+ to K_2^+ , we find that the relative ratios of the interactions $M\text{--He}/\text{He--He}$ get smaller and that the He atoms move further away from the dimer ions due to the increased size of the latter molecules. As a result of these considerations, our findings show that the solvent atoms tend to form clusters where they sit further away from the dimer especially for K_2^+ . Since the collinear approach is clearly favored over the more compact C_{2v} geometry, we can predict that during the growth of $M_2\text{He}_n^+$ clusters the He atoms will tend to localize near either of the alkali atoms, although the actual energy required for packing them around the center of the diatom can only be obtained by actually comparing computed stabilities for the various structures.

We have tried to calculate all possible structures by placing two or more He atoms in different bonding sites. Actual optimizations consist of extensive searches over a few-dimensional internal coordinate space such that the symmetry of the structure is preserved. At every geometry, the potential energy is corrected for the basis set superposition error (BSSE) by the counterpoise procedure.¹⁵ Hence, the optimum geometries may be slightly different from those obtained by standard energy minimization procedures. In this manner, we have generated up to 6 structures for $n=2\text{--}5$ and two structures for $n=1$ and 6. In Fig. 11, schematic drawings

FIG. 11. Structures of the clusters analyzed in the present work. Lighter particles always indicate He atoms.

of these 26 clusters are presented. We have used the nomenclature (nm) for the m th shapes of a cluster with n helium atoms. All calculations were carried out with GAUSSIAN 03.¹⁶

For the Li_2^+ containing clusters, the search over the PES has been carried out using both MP2(full)/cc-pvtz and by MP4(full)/cc-pvqz methods and basis sets. The Li–Li distance is kept frozen at 3.11 Å as in our PES calculation. In terms of optimum geometries from these two sets of calculations, we found only minor differences such that the Li–He distances in MP4 are shorter, especially for the weakly interacting geometries of the C_{2v} case. The valence angles obtained by both methods, however, agreed extremely well. By comparing the relative energies found with the two methods, we decided that the minima searches over the PESs can be safely conducted using the MP2/cc-pvtz method followed by single point energy calculations at the MP4/cc-pvqz level. For example, for structures with $n=1-3$, the differences in the potential energy coming from the two calculations are within $\sim 1 \text{ cm}^{-1}$.

In Table II we report the energetics calculated for all Li_2He_n^+ , Na_2He_n^+ , and K_2He_n^+ clusters. Potential energy values are given in cm^{-1} . For $n=2$, five different structures were tried and two of those were found to be relatively more stable than the others. The global minimum is linear (21) while the structure with C_{2v} symmetry where the diatomic axis bisects the plane of He–Li–He (24) is energetically close to the global minimum. For $n=3$, the global minimum is (31) which is a combination of (21) and (24) structures. There are three more local minima with small energy differences between each other: the first local minimum has C_{3v} symmetry (34), the next one is linear (32), and there is a further structure with two helium atoms lying collinearly along the Li_2^+ axis and the other helium perpendicular to the molecular axis (33). An additional cluster similar to the global minimum but in which all atoms are sitting on the same plane (35) turned out not to be very stable. In all these structures we found that the He atoms try to occupy the external sites along the molecular axis.

For larger clusters, the stable structures can be formed by appropriate combinations of substructures such as linear (L) as in (11), extended linear (EL) as in (25), T shaped (T) as in (24), and a triangular (P) fragment as in (35). The other structures can also be generated by forming n -membered rings (R_n) outside and perpendicular to the Li_2^+ core. In the case of $n=4$, the global minimum (41) is composed of two T-shaped He_2 clusters, although it is not easy to predict the relative ordering of further local minima. The second lowest-lying structure (45) is a combination of a T and EL while in the next one, (44), four He atoms form a square cluster (R_4) perpendicular to the Li_2^+ . Finally two of them are close in energy but located about 400 cm^{-1} above the global minimum. The clusters for $n=5$ and 6 are formed by combinations of T and P fragments as the helium atoms are avoiding the center of Li_2^+ . The global minimum for $n=5$ is T-P and for $n=6$ is P-P. On the other hand, we found that the five-membered ring R_5 is highly unstable.

All the structures discussed above correspond to the classical optimum points along the PES. For a more physical identification of the possibly significant effects of zero-point energy expected in such structures, we have obtained harmonic frequencies at the MP2/cc-pvtz level: those with all positive eigenvalues of the Hessian are identified as classical minima (M in Table II). Among the minima, the structures whose zero-point corrections are less than V can be safely classified as bound quantum structures. In Table II, the second column is the sum of the potential energy and the zero-point energies. Among $M_2\text{He}_n^+$ clusters, all those which have positive definite Hessian are suggested to represent quantum minima. The majority of these clusters yield true minima and the zero-point corrections are well below the dissociation energies. However, one must be careful in evaluating results from this analysis since some of the optimal structures may have imaginary frequencies in the harmonic approximation but the anharmonicity of the PES could cause significant changes especially for those identified as saddle points. Thus,

TABLE II. Potential energy values (V), zero-point energy (harmonic) corrected values ($V+ZPE$), and percentage differences with the two-body value in the same geometry for the $M_2\text{He}_n^+$ clusters. Energies are in cm^{-1} . Structures where the Hessian has no negative eigenvalues are denoted with M.

	$\text{Li}_2^+-\text{He}_n^+$			$\text{Na}_2^+-\text{He}_n^+$			$\text{K}_2^+-\text{He}_n^+$		
	V	$V+ZPE$	$V_2(\% \text{Diff})$	V	$V+ZPE$	$V_2(\% \text{Diff})$	V	$V+ZPE$	$V_2(\% \text{Diff})$
11	-369.1	-34(M)	-377.7(-2.3)	-93.5	41(M)	-93.5(0.0)	-37.6	28	-37.4(0.6)
12	-9.9	129	-11.5(-16.3)	-6.4	58(M)	-6.4(-0.5)	-3.8	42	-3.9(-2.6)
21	-730.6	-189(M)	-755.5(-3.4)	-183.0	26(M)	-186.2(-1.7)	-74.1	19	-74.8(-1.0)
22	-379.0	-33(M)	-389.6(-2.8)	-100.0	43(M)	-100.0(0.0)	-41.3	12	-26.9(35.0)
23	-19.9	130	-23.2(-16.3)	-12.9	58	-12.9(-0.3)	-7.5	61	-7.8(-4.0)
24	-602.3	-59(M)	-610.4(-1.3)	-157.4	21	-164.0(-4.2)	-73.9	34	-81.5(-10.3)
25	-384.6	-21(M)	-404.7(-5.2)	-102.7	57(M)	-111.8(-8.8)	-44.8	36	-55.8(-24.5)
31	-953.3	-210(M)	-987.2(-3.6)	-242.4	-3	-255.4(-5.4)	-109.4	26	-119.0(-8.7)
32	-745.7	-177(M)	-782.2(-4.9)	-192.1	42(M)	-204.8(-6.6)	-81.3	-81	-93.2(-14.7)
33	-740.3	-189(M)	-767.6(-3.7)	-189.3	28(M)	-192.8(-1.9)	-77.8	23	-78.8(-1.3)
34	-816.8	-54(M)	-806.6(1.2)	-226.1	21	-247.5(-9.5)	-116.5	50	-138.1(-18.5)
35	-627.9	-54(M)	-659.8(-5.1)	-174.0	40	-201.0(-15.5)	-82.7	36	-107.1(-29.5)
36	-473.2	-37	-517.7(-9.4)	-156.6	55(M)	-177.1(-13.1)	-91.2	52	-110.2(-20.8)
41	-1164.2	-209(M)	-1219.2(-4.7)	-298.7	-15	-324.1(-8.5)	-143.9	31	-163.1(-13.4)
42	-758.8	-173(M)	-805.6(-6.2)	-201.2	51(M)	-223.1(-10.9)	-88.5	34	-111.3(-25.8)
43	-750.0	-187	-779.9(-4.0)	-195.6	28	-199.5(-2.0)	-81.4	24	-82.8(-1.7)
44	-817.3	109	-752.6(7.9)	-238.5	38	-274.3(-15.0)	-146.4	74	-176.6(-20.6)
45	-968.1	-199(M)	-1013.8(-4.7)	-252.5	22	-275.0(-8.9)	-116.6	32	-137.4(-17.8)
46	-978.5	-204(M)	-1037.0(-6.0)	-260.1	24	-294.1(-13.1)	-119.9	48	-153.7(-28.2)
51	-1358.0	-193(M)	-1414.4(-4.2)	-359.4	-7	-404.9(-12.7)	-184.9	54	-219.7(-18.8)
52	-1172.0	-215	-1231.8(-5.1)	-309.2	24	-336.4(-8.8)	-147.6	35	-167.3(-13.4)
53	-1186.4	-215(M)	-1266.7(-6.8)	-318.7	28	-365.2(-14.6)	-154.1	57	-197.9(-28.4)
54	-1173.1	-186(M)	-1210.1(-3.2)	-318.3	19	-355.9(-11.8)	-158.5	56	-194.1(-22.5)
55	-530.3	209	-580.9(-9.5)	-202.1	61	-261.7(-29.5)	-156.6	97	-205.1(-31.0)
61	-1538.1	-200(M)	-1611.9(-4.8)	-419.0	-3	-485.5(-15.9)	-225.0	80	-276.3(-22.8)
62	-1213.3	-203	-1315.6(-8.4)	-331.3	20	-399.3(-20.5)	-164.6	239	-232.6(-41.3)

the present correction for ZPE provides only a qualitative indicator for more complicated quantum effects.

The charge distributions on the dopant and solvent atoms clearly show that the single charge is basically localized on Li_2^+ ; however, as the cluster grows there is a slight charge transfer from Li_2^+ to helium atoms. The total charge transfer (Q) is always a maximum for the global minima of each n (in fact, there is a very strong correlation between the strength of the interaction potential and Q which has a linear dependence on n given by $Q=0.04n$ in a.u.). On the other hand, spin localization on Li_2^+ does not display any regular feature along the cluster series.

For the Na_2^+ containing clusters we have calculated the same optimum structures as described above and have kept the same nomenclature. The Na–Na distance is frozen at 3.69 Å, a value obtained by optimization with MP4/cc-pvqz. First of all we carried out a comparative study of various basis sets in order to find the most economical set which would reliably yield energy calculations of larger clusters. In Table III, we present the potential energy values of three clusters (11), (21), and (24) with different mixed basis sets. Note that the geometries used in this table are not optimum geometries and therefore the energies differ slightly from those reported in Table II although the name of the structure is the same.

Since cc-pv5z is the most extensive basis among those we have employed here and yields the largest potential energy values, we sorted these basis sets according to their decreasing energy. For the linear Na_2He_n^+ all basis sets were

compared, and for the two structures of Na_2He_n^+ a selected set of calculations were repeated. Considering also the disk and CPU time requirements, we have concluded that a mixed basis set of cc-pv5z for He and 6-31(3df) for Na atoms (from now on denoted as the mixed basis) gives the optimum results in terms of the efficiency of the calculations. The restricted optimizations and frequency calculations were carried out using the MP2(full)/cc-pvtz method while the single point energy calculations are with the MP2(full)/mixed one. The potentials obtained with this method are compared for several structures to those obtained from optimization with the mixed basis. The agreement is again very good, with errors of less than 2 cm^{-1} .

The major difference between Li_2He_n^+ and Na_2He_n^+ is the strength of interactions which is uniformly reduced by 75%: The global minima of the Na containing clusters are the same as those in the Li_2He_n^+ ones. In fact, the relative energy of all clusters follows the same order in both sets. A consequence of this finding is that the number of quantum-corrected minima is much smaller for the Na containing clusters: There are only four structures with ZPE less than the potential depth but they all have at least one negative force constant. Those structures with frequencies which are real do not seem to support a single vibrational level at the harmonic approximation. However, an accurate description of the correct zero-point energy values might be obtained only from exact quantum calculations such as quantum Monte Carlo treatments (e.g., see Ref. 10). Charge localization, though

TABLE III. Potential energies for three selected structures of Na_2He_n^+ obtained with different basis sets. The potentials are corrected for BSSE and are given in units of cm^{-1} .

He basis	Na basis	(11)	(21)	(24)
cc-pv5z	cc-pv5z	-101.6	-199.2	-169.7
ccpv5z	6-31++(3df)	-94.8	-185.7	...
ccpv5z	6-31(3df)	-94.5	-185.2	-154.0
cc-pvqz	cc-pvqz	-88.8	-173.8	-145.8
ccpv5z	6-311(3df)	-88.8	-173.0	...
ccpvqz	6-31++(3df)	-86.7	-169.5	...
ccpvqz	6-31(3df)	-86.4	-169.0	-137.1
ccpvqz	6-311(3df)	-79.7	...	...
ccpv5z	6-31(d)	-79.0	-153.7	-128.6
ccpv5z	6-311(d)	-76.4	-148.4	...
ccpv5z	LanL2DZ	-69.8	-135.9	-109.3
ccpvqz	6-31(d)	-68.5	-141.6	-108.6
ccpvtz	6-31(3df)	-67.6	-131.4	-101.9
ccpvqz	6-311(d)	-65.7	...	...
cc-pvtz	cc-pvtz	-62.2	-120.6	-97.7
ccpvqz	LanL2DZ	-57.3	-111.1	-87.2
ccpvtz	6-31(d)	-48.2	-92.3	-73.1
ccpvtz	LanL2DZ	-36.9	-70.7	-50.9
6-31++(3df)	6-31++(3df)	-23.7	-12.1	...
6-31(d)	6-31(d)	-23.5	-42.7	...
6-31(3df)	6-31(3df)	-19.1	16.4	...
6-311(d)	6-311(d)	13.0	30.0	...

much weaker than that of Li_2He_n^+ , follows the same trends, i.e., the more stable the cluster, the larger is the charge transfer. The linear relation still holds but now yields a smaller slope $Q=0.01n$ (in a.u.).

For the K_2^+ impurity, we have used the above optimized mixed basis both for structure search and for the frequency calculations. The K-K distance is frozen at the experimental geometry of 4.4 Å.¹⁴ Following the trends already observed from Li_2He_n^+ to Na_2He_n^+ , the interactions are now even weaker. Even though the stability order is almost the same, potential energies are about half of those in Na_2He_n^+ , the only exception being K_2He_4^+ that has the structure (44) where a square He_4 is perpendicular to the main K_2^+ axis and is the global minimum [the energy difference between this structure and the other minimum (41) is around 2 cm^{-1}]. The frequency analysis further shows that none of these clusters has a true minimum in the harmonic approximation. These are, however, saddle points of very high order where the zero-point corrections lose their physical meaning. The charge transfer is found, as expected, to be smaller and approximately half of that shown by Na_2He_n^+ .

Finally we present in Table IV several key geometrical parameters in order to allow for a comparison between the different structures. The second column shows representative values for the definition of the distances and angles. In K_2^+ containing clusters the dependence of He-M distances on the size of the cluster is weaker than in the other two. In the cases of Li_2^+ or Na_2^+ impurities, instead, the He atoms could get closer to the dimer and the resulting crowding of He atoms in such clusters makes the distances slightly larger as n gets higher.

TABLE IV. Final geometrical parameters (distances in Å and angles in degrees) for different cluster structures.

	Structure	Li	Na	K
$R(\text{He-M})$	11	2.02	2.69	3.32
	12	5.20	5.80	6.60
	24	2.05	2.76	3.34
	34	2.09	2.80	3.35
	44	2.17	2.97	3.35
(He-M-M)	35	4.35	5.16	5.40
	24	140	148	153
	34	133	143	148
	44	124	135	140

V. TESTING THE VALIDITY OF THE SUM-OF-POTENTIAL APPROXIMATION

In Table II we have also reported the percentage energy difference between the *ab initio* (AB) values given in columns 2, 6, and 10 and the one we can obtain by adding together all two-body (2B) contributions. The formula we have used is

$$\% \text{Diff} = \frac{V_{\text{AB}} - V_{2\text{B}}}{V_{\text{AB}}} 100, \quad (6)$$

where $V_{2\text{B}}$ is given by the following expression:

$$V_{2\text{B}} = \sum_n V_{\text{A}_2^+-\text{He}} + \sum_{n>k} V_{\text{He-He}}, \quad (7)$$

where the He-He interaction is the interaction given by Aziz *et al.*²⁵ and the A_2^+-He interaction is given by the potentials discussed in Sec. II. As we can see from the values reported in Table II, the difference between the *ab initio* value and the sum-of-potential approximation increases with increasing cluster size and, on the average, also when going from Li_2^+ to K_2^+ -doped species, even if the trend is opposite for some of the structures. The large difference seen for the $\text{M}_2^+-\text{He } C_{2v}$ structures is due to the relative weakness of the potential wells for such geometries and to the sensitivity of its value to the basis set used in the *ab initio* calculations (in the optimization process we have used the cc-pvqz, while in the PES of Sec. II the cc-pv5z basis has been employed). The largest differences, in fact, are given by the structures which present the ring of helium atoms on one side of the molecule (i.e., 34, 44, and 55). The larger errors that one sees with the K_2^+ -doped clusters are mainly due to the fact that the numerator in Eq. (6) is strongly affected by the *ab initio* values chosen to describe the He-He interaction. The one that we obtain from solely *ab initio* estimates is not as accurate or as attractive as the empirical interaction provided by Ref. 25. It then follows that most of the two-body energies turn out to be greater than those obtained from *ab initio* calculations, especially for Na- and K-doped systems. On the other hand, we also qualitatively see that the sum-of-potential energies are the lowest for the same structural minima found by *ab initio* calculations, thereby providing the same minimum energy structures and the same sequential ordering of relative stabilities. This therefore means that, at least for the Li_2^+He_n clusters, one can employ the sum-of-potential modeling of

the forces to analyze larger clusters with a good reliability of the final results. With the same token it is unfortunately more difficult to assess the validity of the sum-of-potential approximation for Na_2^+ - and K_2^+ -doped clusters because while we expect three-body effects to increase slightly due to larger molecular sizes, the much smaller interaction present in such species makes the comparison extremely sensitive to the calculation schemes one employs. Since the He–He well depth in the sum-of-potential approach is more than twice deeper than the one produced by the MP2/mixed calculations, the lower interaction values often given by the sum-of-potential approximation can be related to that artifact of the scheme.

VI. PRESENT CONCLUSIONS

The work reported in the present paper has been directed to the study of the interaction forces between a series of different alkali dimer ions (Li_2^+ , Na_2^+ , and K_2^+) and either a single He atom or a small number of them. The motivation for this analysis has come from the strong interest in using helium nanodroplets as cold matrices for a broad variety of molecular dopants¹ and in comparing their modified behavior and structures upon ionization or, in general, upon acquiring positive or negative charges.^{26,27} The confirmed evidence that helium aggregates are highly quantum, weakly interacting objects^{3,4} suggest, in fact, that one may profitably employ a sum-of-potential approximate description of the overall interaction even in situations where the dopant species is a cation that gets rapidly solvated.⁷ Thus, an accurate knowledge of such potentials between the single He species and the molecular dopant can provide a very useful starting point for the study of cluster structures and solvation shells (e.g., see also Ref. 28). We have further provided analytic fits of the three PESs for the title systems (which are available on request from the corresponding author) and analyzed the ensuing structures of the bound states supported by such potentials. Finally, we have also described as accurately as possible the most likely structures of the smaller clusters resulting from the presence of more helium atoms surrounding the dopant ion. Whenever possible, we have also tried to estimate the large quantum effects which exist in such species. The following general features could be extracted by the spatial and energy characteristics of the bound states.

1. The strength of the ionic interactions markedly decreases from Li_2^+ to K_2^+ and becomes more repulsive along that series (e.g., see Fig. 2).
2. As expected, the ZPE is very large for all three systems and, although it decreases from Li to K, it constantly constitutes for all of them a substantial percentage of the potential wells: 33% for Li_2^+ , 48% for Na_2^+ , and 54% for K_2^+ .
3. The number of bound states in the smallest complexes decreases along the series and all three systems exhibit a few states near dissociation which are above the inversion barrier. Such states have density profiles that depend on the parity of the rotational wave function of the dimer ion and therefore on its nuclear spin symmetry. The states with energies lying below the barrier

have instead a very similar shape and energy and give rise to a doublet structure (with separations of the order of 10^{-4} cm^{-1}).

4. The systems further show very large amplitude motions, both as stretching and bending modes, in their lower states but rapidly undergo passage to nonregular maps of their wave functions as one moves to the excited states.

In the case of the clusters with $n > 1$ the stability of clusters follows the order $\text{Li}_2\text{He}_n^+ > \text{Na}_2\text{He}_n^+ > \text{K}_2\text{He}_n^+$. Since the clusters we have investigated are not large enough to include a second solvation shell, it is possible that the potential energy of the global minima can be expressed approximately as linear function of the number of He atoms. For K_2He_n^+ , due to the rather large size of the K atoms, this is the case and the total potential energy of the global minima can be obtained as $V = n \times 37 \text{ cm}^{-1}$. For Li and Na containing clusters, the interaction energy is no longer a simple scalable function since the He atoms can get closer to the molecule and the interactions between He atoms start to play an important role in guiding the stability.

In the case of the small aggregates with $n > 1$, our calculations show that the Li_2^+ dopant forms stable structures with He atoms also when estimating the quantum effect of the ZPE within the harmonic approximation. On the other hand, in the case of Na_2^+ and K_2^+ , the harmonic approximation indicates that only a small number of He atoms can be attached to the former dimer and none binds to the latter although it is very likely that a correct treatment of quantum effects would provide bound structures of all the clusters. Apart from the differences in the magnitude of well depths, the optimum points along the three PESs are very similar, and collinear structures are always favored when the number of helium atoms is that small. Hence, the cationic species from the alkali dimers are expected to become rapidly solvated into the droplet, in contrast to what has been found for the neutral counterparts of the alkali oligomers.^{10,11,29–31} The present study can therefore provide some initial information on how the structuring of this quantum solvent could be guided by the features of the corresponding PESs with the cationic impurities and by their interplay with the pure solvent interactions.

We have previously shown that for ionic impurities in He droplets,^{13,32} the potential energy can be obtained with reasonable accuracy from additive potentials. A similar analysis has been carried out here by comparing *ab initio* many-body energies with the sum-of-potential ones. The analysis has shown that, while the two approaches are qualitatively in agreement in finding and locating the minimum structures among the various possibilities, they provide similar values of the interaction only for Li_2^+ dopant. On the other hand, in all three systems we find that the relative stability sequence is preserved when using the sum-of-potential approximation.

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