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Abstract

We present variational calculations on systems containing a few boson helium atoms attached to electronically excited atomic and molecular helium anions He^{*-} and He_2^{*-} , and characterise their structures and energetics. Previously reported high level *ab initio* results [Huber, S. E.; Mauracher, A. *Mol. Phys.* **2014**, *112*, 794] to describe the interactions between excited (metastable) anions and a neutral He atom have been employed. For the case of the atomic species He^{*-} , the corresponding interaction with He suggests large anharmonicity effects due to the presence of a deep well of $\sim 17,500 \text{ cm}^{-1}$ at short distances, together with a more external shallow secondary well of $\sim 4 \text{ cm}^{-1}$, both supporting bound levels. Moreover, when a sum of pair-wise interactions is assumed to describe the full PES corresponding to the presence of several neutral He atoms, geometrical constraints already predict the complete solvation of the anionic impurity by six helium atoms, giving rise to a bi-pyramidal structure. In turn, for the anisotropic weak interaction $\text{He}-\text{He}_2^{*-}$, where the anionic dimer is considered as a rigid rotor, the obtained structures show the tendency of the helium atoms to pack themselves together and largely far away from the dopant, thereby confirming the heliophobic character of He_2^{*-} .

I. Introduction

The study of the fundamental properties of molecules, clusters, and molecular complexes at low and very low temperatures presents clear advantages. On the one hand, the number of accessible molecular states could be reduced by various orders of magnitude, allowing a much less ambiguous assignment process. Furthermore specific features of the systems like the existence of tiny barriers and tunneling processes gains importance and may eventually determine the shape of the overall interactions or the evolutions of the processes under study. The use of helium atoms has proven to be a very useful resource in this range of temperatures and within the context of the structural studies: the choice of this inert gas for sympathetic cooling of a broad range of molecules has, in fact, been found to be important since pioneering studies,¹ and the combination of molecular dopants (picked up by a cold cluster of either ^3He or ^4He atoms) with spectroscopic analysis,^{2,3} has turned out to be a winning arrangement for low-T structural and dynamical studies.^{4,5}

In gas phase, the atomic anion He^- , with a long lifetime of $\sim 360 \mu\text{s}$, has been reported in different experiments almost a century ago, see Ref.⁶ and references therein. Also, long-lived metastable He_2^- molecular ions produced from He_2^+ by two-step electron capture in an alkaline vapor target were for the first time observed by Bae *et al.*⁷ Its structure was studied via autodetachment spectroscopy,⁸ while a lifetime of $\sim 135 \mu\text{s}$ was estimated using a heavy-ion storage ring.⁹ In turn, charged species, especially cations,¹⁰ embedded in helium droplets at a low temperature regime have been the subject of careful investigations over the past years. Some of the interest of studying anions immersed in these clusters on the other hand deals with the understanding of the mechanisms of charge displacement within a helium environment. In this sense, besides free electrons attached to large clusters, the presence of atomic and molecular helium anions inferred from resonances in experimental spectra¹¹ leads to suggest possible role of these ions as interesting charge carriers under superfluid conditions. Instead of ionization by interaction between external electrons and neutral He droplets, the formation of helium anions seems to respond to a two-step mechanism involving the electronic excitation to metastable states.^{11–13} Thus for example, the He^{*-} ion, $\text{He}(1s2s2p^4P)$, is formed by means of the following pathway:

where the energy contained in the electron penetrating into the cluster is sufficient to overcome the penetration energy requirements (1.2 eV)¹⁴ and to lead He from its ground state to the first excited electronic state $\text{He}(1s2s \ ^3S)$, He^* . Separate bubbles containing He^* and a zero kinetic energy electron collide to finally form, He^{*-} ,^{12,15–17} originally detected as a fast ion in bulk helium as reported in Ref.¹⁸ Its heliophilic character¹² and its large mobility through the helium medium (although this property is not unanimously accepted) would make this atomic anion a good candidate to explain the formation of ionic dopants inside the helium droplet, a mechanism which would compete with previous assumptions of migration of bubbles containing electrons to the neutral impurities.^{19,20} The molecular helium He_2 anion ($1\sigma_g^2 1\sigma_u 2\sigma_g^1 \pi_u^4 \Pi_g$), hereafter He_2^{*-} , exhibits on the contrary a heliophobic behaviour inside the cluster, with a marked tendency to migrate towards the surface. Its formation at the low temperature regime existing in the cluster is strongly affected by the existence of barriers, and seems to be the result of a dimerization of the ground state He with $\text{He}(1s2p \ ^3P)$ and $\text{He}(1s3p \ ^3P)$.¹² The energy of these excited states plus the penetration energy of the incident electron would lead to the formation energy of He^{*-} and He_2^{*-} of 22.1 eV and 24.2 eV, respectively.^{12,13} Metastable states of both atomic and diatomic helium²¹ and accurate *ab initio* calculations of the CCSD(T) type to describe the interaction of He^{*-} and He_2^{*-} with He atoms have been recently reported.¹⁷ Energies for the $\text{He}(^1S)\text{--}\text{He}^{*-}(^4P)$ and $\text{He}(^1S)\text{--}\text{He}_2^{*-}(^4\Pi_g)$ interactions for different interparticle distances and angular orientations were calculated. The study of Ref.¹⁷ also included a detail analysis of the different behaviour of both He^{*-} and He_2^{*-} immersed in the helium cluster.

Path integral Monte Carlo (PIMC) calculations at low temperature (0.4 K) on He_N clusters, $N \leq 32$, doped with the above mentioned anionic species have been recently reported.²² The $\text{He}_N\text{--}$

He^{*-} clusters with $N > 6$ display a structure defined by a bipyramidal core composed by six helium atoms around the atomic anion, whereas the rest of surrounding He atoms form a dimple around that initial cage. On the contrary, the structures obtained and analyzed for the He_N-He₂^{*-} clusters show the dopant located outside the helium droplet. In the present paper, we focus on these kind of systems by considering clusters containing just a few helium atoms for which variational calculations are feasible. We try in this way to get some additional insight on the fundamental physics of the structure and energetics of these small clusters, as well as the underlying interactions. The paper is organized as follows: Section 2 shows the general characteristics of the *ab initio* potential energy surfaces (PES's), while Section 3 briefly outlines the main details of the variational methods employed in this work. Section 4 presents and analyzes our computational results for the two anionic species accounted for, while the final Section 5 reports our present conclusions.

2. Potential Energy Surfaces

Electronic structure calculations on the molecular anion He₂^{*-} were first performed by Michels^{23,24} by means of configuration-interaction wave functions. Also, using high-level coupled-cluster methods, structure and autodetachment spectra were reported.²⁵ Recently, accurate *ab initio* calculations of the CCSD(T) type²⁶ were performed by Huber and Mauracher¹⁷ to describe the He-He^{*-} and He-He₂^{*-} interactions. 196 points equally spaced in the interval [0.5-20] Å were considered for the atomic anion. For the latter, the anion was frozen at its equilibrium distance of ~ 1.1 Å, as established along the calculations for the former. A dense grid of 76 radial points in the interval [5-20] Å were considered for 16 orientations in the range $[0-\pi/2]$ of the He with respect to the anionic species and thus accounting for the anisotropy of the interaction.

For systems containing several He atoms plus an anionic species, the full PES employed in the present work has been written as the sum of the corresponding pair-wise He-He and He-anion interactions. The He-He interaction was described using the potential by Aziz and Slaman²⁷ with a well depth of ~ 7.59 cm⁻¹ and a equilibrium distance of ~ 2.97 Å.

2.1. He-He^{*-} interaction

Figure 1 displays the interaction of a neutral He atom and the He^{*-} anion, where the whole curve has been lowered by ~ 19.81 eV, its actual asymptotic limit. As stated in Ref.¹⁷ the He^{*-}-He system at the global potential minimum displays the structure of a He₂⁺ core and a diffuse electronic shell due to the two electrons occupying σ and π orbitals. The bonding of He^{*-} with a neutral He atom appears to be mainly of ionic character, i.e., non directional. After that structure, the potential becomes much weaker thereby sampling the outer, secondary minimum. It therefore appears as being originated from the crossing of a cationic curve (similar to that of He₂⁺) and a repulsive state correlating at long distances with He(¹S) + He (1s2s2p ⁴P), giving rise to an intermediate barrier of ~ 600 cm⁻¹ between the inner deep well of $\sim 17,500$ cm⁻¹ and the outer shallow one of ~ 4 cm⁻¹.

In that figure we also depict the states supported by this potential: 13 ($0 \leq v \leq 12$) are placed on the inner region, while two very weakly bound levels ($v = 13, 14$) are located on the region of the secondary well (see the inset in Figure 1. They were obtained through an efficient mixed Truhlar and Numerov-Cooley procedure²⁸ accounting for 100,000 points equally spaced in the interval [0.5-1000] Å and are listed in Table 1. As mentioned above, the structure exhibited by this interaction envisages large vibrational anharmonicity effects when several He atoms are interacting with the atomic anion. So, as we will show below, these effects are already clear for a system like He₂-He^{*-}, where all the possible combinations of those 15 states can contribute to the three-body bound levels.

Moreover, and under the assumption of pair-wise interactions, an evolutive algorithm as well as PIMC calculations at 0.4 K²² predict the formation of a quasi-rigid structure formed by 6 He atoms located at the vertexes of a squared-basis bipyramid with the anion placed at the center, the corresponding distances He-anion being of ~ 1.2 Å, i.e., its equilibrium distance, while the He-He distances are of ~ 1.7 Å. The bonds between the impurity and the atoms participating in the bipyramid structure have their physical origin in the charge-polarization undergone by the tightly bound electrons of the He atoms due to the presence of the He^{*-} system. This inner solvating

cage would be then formed by an ensemble of He^+ cations sharing an electronic cloud. This “chemically bound molecular” configuration existing at the shorter distances shifts however to a “polarisation-bound complex” at larger distances beyond the potential barrier exhibited by the He^{*-} -He potential around $\sim 2.5 \text{ \AA}$. Additional He atoms therefore sample a much weaker potential due to the screening induced by the presence of the inner core of six atoms surrounding the impurity and move further out when encountering the shallower local potential minimum located at $\sim 7 - 8 \text{ \AA}$. The formation of a stable and rigid helium cage around the atomic anion is consistent with the previously suggested heliophilic character for He^{*-} .¹²

Table 1: Vibrational energies of the He-He^{*-} system.

v	Energy (cm ⁻¹)
0	-16229.3295
1	-14503.5674
2	-12853.3525
3	-11277.7340
4	-9773.8218
5	-8331.3109
6	-6934.3917
7	-5582.5870
8	-4291.5784
9	-3075.2984
10	-1951.4393
11	-947.2040
12	-100.9499
13	-1.2657
14	-0.0054

Note that the anisotropy of the $\text{He}(^1\text{S})\text{-He}^{*-}(^4\text{P})$ system induced by the orientation of the unpaired electron p-orbital is not accounted for, and for He atoms out of the nodal plane the pairwise potential could overestimate the He-He^{*-} attraction.

2.2. He-He₂^{*-} interaction

The interaction potential between the He atoms and the diatomic anion He_2^{*-} depends in turn both on the distance R from the center of mass of the anion and the neutral atom, and on the angle

θ formed between the position vector of the He atom and the bond direction within the He_2^{*-} impurity:

$$V_{\text{He-He}_2^{*-}}(R, \cos \theta) = \begin{cases} \sum_{n=4}^8 C_n(\cos \theta)/R^n & R > R_0 \\ \sum_{n=4}^8 C_n(\cos \theta)/R_0^n & R \leq R_0 \end{cases} \quad (1)$$

with a cutoff value of $R_0 = 6 \text{ \AA}$ and where

$$C_n(\cos \theta) = \begin{cases} -\mathcal{C}_4 & n = 4 \\ \sum_{\ell=0}^5 a_{\ell n} \cos^\ell \theta & n > 4 \end{cases} \quad (2)$$

where $\mathcal{C}_4 = 11363.2878 \text{ \AA}^{-4} \text{ cm}^{-1}$. The leading term at long distances, $-\mathcal{C}_4/R^4$, describes properly the corresponding charge-induced dipole interaction. Table 2 shows the values of the corresponding parameters in the expansion of Eq. (2). The interparticle distance within the He_2^{*-} unit is taken as the corresponding to the minimum of the He-He* potential, $\sim 1.1 \text{ \AA}$, (see Figure 1). Figure 2 shows the *ab initio* points of Ref. ¹⁷ for ten values of the θ angle in the range $[0, \pi/2]$, in comparison with the analytical fit as expressed in Eq. (1).

Table 2: Values of the $a_{\ell n}$ coefficients for the expansion in Eq. (2) for the $V_{\text{He-He}_2^{*-}}(R, \cos \theta)$ potential describing the interaction between the diatomic anion impurity He_2^{*-} and the He atoms.

	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	$\ell = 5$
$a_{\ell 5} (10^7 \text{ \AA}^{-5} \text{ cm}^{-1})$	0.2055	0.1190	-1.2209	3.0799	-3.8827	1.7342
$a_{\ell 6} (10^9 \text{ \AA}^{-6} \text{ cm}^{-1})$	-0.0904	-0.0417	0.4457	-1.0453	1.2853	-0.5639
$a_{\ell 7} (10^{10} \text{ \AA}^{-7} \text{ cm}^{-1})$	0.1181	0.0494	-0.5404	1.2033	-1.4418	0.6200
$a_{\ell 8} (10^{10} \text{ \AA}^{-8} \text{ cm}^{-1})$	-0.4109	-0.1964	2.1065	-4.6991	5.4955	-2.3137

3. Variational treatments

3.1. He₂–He^{*−}

The Hamiltonian describing a He₂–He^{*−} triatomic system can be written in relative coordinates $\{\mathbf{R}_k\}$, after separation of the center of mass motion, as^{29,30}

$$H = \sum_{k=1}^2 \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R_k^2} + \frac{\mathbf{l}_k^2}{2\mu R_k^2} + V_{\text{He}^{*-}-\text{He}}(R_k) \right] + V_{\text{He}-\text{He}}(R_1, R_2, \cos\gamma) - \frac{\hbar^2}{m_{\text{He}}} \nabla_{\mathbf{R}_1} \cdot \nabla_{\mathbf{R}_2}, \quad (3)$$

where $\mathbf{R}_k$ are the vectors from the He^{*−} anion to the different He atoms, $\mathbf{l}_k$ are the angular momenta associated with $\mathbf{R}_k$, μ is the reduced mass of the He^{*−}–He system (here we have considered that the mass of the anion and that of the neutral atom are identical), and $\cos\gamma = \mathbf{R}_1 \cdot \mathbf{R}_2 / R_1 R_2$. The last two terms in Eq. (3) describe the He–He interaction, and a kinetic energy coupling which has its origin in the use of non-Jacobi coordinates, respectively. In a space-fixed coordinate system, we consider the following basis functions:

$$\phi_{q_1 q_2}^{JM}(\mathbf{R}_1, \mathbf{R}_2) = g_{m_1}(R_1) g_{m_2}(R_2) \mathcal{Y}_{\ell_1 \ell_2}^{JM}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2), \quad (4)$$

where the g_{m_i} functions, associated with the anion–He vibrations, are the numerical eigen-functions above mentioned for the dimer anion. In Eq. (4), $\mathcal{Y}_{\ell_1 \ell_2}^{JM}$ are angular functions in the coupled representation,

$$\mathcal{Y}_{\ell_1 \ell_2}^{JM}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2) = (-1)^J \sqrt{2J+1} \sum_{\omega} \begin{pmatrix} \ell_1 & \ell_2 & J \\ -\omega & \omega - M & M \end{pmatrix} Y_{\ell_1 \omega}(\theta_1, \phi_1) Y_{\ell_2 M-\omega}(\theta_2, \phi_2), \quad (5)$$

where $\hat{\mathbf{R}}_k = \mathbf{R}_k / R_k = (\theta_k, \phi_k)$ are unit vectors, $\begin{pmatrix} \ell_1 & \ell_2 & J \\ -\omega & \omega - M & M \end{pmatrix}$ are 3- j symbols, and $Y_{\ell_k \omega}$ are spherical harmonics. J is the quantum number associated with the total angular momentum $\mathbf{J} = \mathbf{l}_1 + \mathbf{l}_2$ with third component M , and ℓ_k and m_k ($k=1, 2$) are quantum numbers associated with the angular momenta $\mathbf{l}_k$ and the anion–He vibrations, respectively, and are collected into a set of quantum

numbers $\{q_k\} = \{m_k \ell_k\}$. Further, one builds up a symmetry-adapted basis set of functions:

$$\psi_{q_1 q_2}^{JM\epsilon\kappa} = [2(1 + \delta_{m_1 m_2} \delta_{\ell_1 \ell_2})]^{-1/2} [\phi_{q_1 q_2}^{JM} + \epsilon \kappa (-1)^J \phi_{q_2 q_1}^{JM}], \quad (6)$$

which are eigenfunctions of $\mathcal{E}^*$, the inversion, and $\mathcal{P}$, the permutation of the He atoms, with eigenvalues $\epsilon = (-1)^{\ell_1 + \ell_2}$ and κ , respectively.³¹ Matrix elements of the Hamiltonian of Eq. (3), as well as expressions for probability distributions of the variables R ($R = R_1$ or R_2), $\cos\gamma$, or R_{12} , the He–He distance, can be found in Ref.³²

For several neutral He atoms, as it was mentioned above, recent PIMC calculations²² predict the formation of a bipyramid structure with the anion on the center and 6 He atoms in the vertices, *i.e.* a He_7^{*-} core. We have simulated this situation by considering the core as a point, of mass $= 7 \times m_{\text{He}}$, and interacting with a He atom as $6 \times V_{\text{He-He}} + V_{\text{He-He}^{*-}}$. In this way, calculations for $\text{He}_N\text{-He}_7^{*-}$, $N = 1, 2$, were also carried out.

3.2. $\text{He}_2\text{-He}_2^{*-}$

Using again relative coordinates $\{(\mathbf{r}, R_k)\}$, with $\mathbf{r}$ being the vector for the interparticle distance in the anion, and $\mathbf{R}_k$ the vectors from the center of mass of the anion to the different He atoms, the Hamiltonian which describes the system is an extension of that shown in the precedent subsection:^{32,33}

$$H = H^d + \sum_{k=1}^2 H_k^t(\mathbf{R}_k, r) + V_{\text{He-He}}(R_1, R_2, \cos\gamma) - \frac{\hbar^2}{2m_{\text{He}}} \nabla_{\mathbf{R}_1} \cdot \nabla_{\mathbf{R}_2}, \quad (7)$$

where H^d is the He_2^{*-} Hamiltonian, and H_k^t , ($k = 1, 2$) are He– He_2^{*-} triatomic Hamiltonians containing the atom-diatom anion intermolecular potential, W , which depends both on the pair of (R_k, r) distances and on the angle θ_k between the $\mathbf{R}_k$ and $\mathbf{r}$ vectors. For a complex containing just a couple of helium atoms, an “exact” variational treatment can be readily applied.^{32,34–36} In the present work, the anionic dimer is kept fixed at its equilibrium distance, *i.e.*, it is considered as a rigid rotor, and consequently its Hamiltonian, H^d , reduces to a rotational term $B_e \mathbf{j}^2$, where B_e is the rotational constant and $\mathbf{j}$ is the dimer rotation operator. Also, the atom-diatom anion

intermolecular potentials depend only on the corresponding atom-anion center of mass distance and the relative orientation, see Figure 2. Further, electronic spin effects are taken to be of minor relevance and have been neglected,^{37,38} *i.e.*, the anion has been considered as a pseudo- $^1\Sigma$ partner. Essentially, choosing a body-fixed (BF) frame with the Z^{BF} axis parallel to $\mathbf{r}$, and introducing the quantum numbers associated with the helium orbital angular momentum $\mathbf{l}_k$, ℓ_k , and the He-He $_2^{*-}$ vibration, m_k , collectively denoted by $\{q_k\} = \{\ell_k m_k\}$, ($k=1, 2$), the basis functions are expressed as³²

$$\Phi_{q_1 q_2 L \Omega}^{JM}(\hat{\mathbf{r}}, \mathbf{R}_1, \mathbf{R}_2) = f_{m_1}(R_1) f_{m_2}(R_2) \mathcal{W}_{\ell_1 \ell_2 L \Omega}^{JM}(\hat{\mathbf{r}}, \hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2), \quad (8)$$

where L is the quantum number associated with the total orbital angular momentum $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$, and J is the quantum number associated with the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{j}$ with third component M and Ω on the space fixed and BF frames, respectively. The angular functions $\mathcal{W}_{\ell_1 \ell_2 L \Omega}^{JM}$, which depend on the diatomic orientation $\hat{\mathbf{r}} \equiv (\theta_r, \phi_r)$ with respect to a space-fixed reference system, and on the orientations $\hat{\mathbf{R}}_k \equiv (\theta_k, \phi_k)$ in the BF frame can be expressed as combinations of Wigner rotation matrices and spherical harmonics.^{32,36} The f_m are radial functions associated with the He-anion stretching motion which are numerically obtained as follows:^{36,39,40} at different fixed orientations $\{\theta_n\}$, one looks for just the ground energy level, w_0 , of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + W(R, r_{eq}, \theta_n) - w_0(\theta_n) \right] \phi_0(R; \theta_n) = 0, \quad (9)$$

and the $\phi_0(R; \theta_n)$ eigen-functions are further orthogonalized through a Schmidt procedure leading to an orthonormal set of $\{f_m(R)\}$ functions. The total wavefunction is expanded in a symmetry-adapted basis set composed of functions Eq. (8) which takes into account the relevant symmetry operators of the system, that is the total inversion $\mathcal{E}^*$, the permutation of the He atoms $\mathcal{P}_{12}$, and for a homonuclear dopant, the exchange of diatomic nuclei $\mathcal{P}_d$.^{32,34} Finally, the corresponding Hamiltonian matrix is diagonalized by using standard routines⁴¹ or iterative algorithms⁴² depending on its size.

In order to gain some insight on the evolution of helium arrangements when changing the

cluster size, the above tetra-atomic model has been extended for systems containing a few more helium atoms, $N > 2$, by considering instead of the Hamiltonian of Eq. (7), the following effective Hamiltonian:^{39,40}

$$H^{eff} = H^d + \frac{N}{2} \sum_{k=1}^2 H_k^t(\mathbf{R}_k, r) + \frac{N(N-1)}{2} \left[V_{\text{He-He}} - \frac{\hbar^2}{2m_{\text{He}}} \nabla_{\mathbf{R}_1} \cdot \nabla_{\mathbf{R}_2} \right], \quad (10)$$

which accounts for N tri-atomics grouped into $N/2$ identical tetra-atomics and $\binom{N}{2}$ identical He-He interactions. Note that this term increases quadratically with the number of helium atoms while the former does it linearly.

4. Results

In the calculations presented here we used a mass for the He (no matter if neutral or anionic) $m_{\text{He}} = 4.00260$ amu. For variational calculations, a radial grid of 100,000 points in the R range $[0.5 - 1000]$ Å was employed to solve numerically Eq. (9) using a mixed Truhlar and Numerov-Cooley procedure.²⁸ Ten equally spaced values of θ_k in the interval $[0, \pi/2]$ were included. Expansions of the He-He and He-He₂^{*-} analytical interactions in Legendre polynomials were carried out by considering 101 Gauss-Legendre points in the $[0, \pi]$ and $[0, \pi/2]$ intervals, respectively. To avoid spurious results, a cutoff of $1,000 \text{ cm}^{-1}$ was imposed on the different interactions. For the complexes involving He^{*-}, a total angular momentum $J = 0$, even values of ℓ_i up to 15, and even values of the inversion and the exchange of He atoms were considered. As regards the vibrational basis, and taking advantage of the spatial separation between inner and outer wave-functions, see Figure 1, we used 3 eigen-states of the He-He^{*-} interaction which will be further specified attaining a convergence within a few cm^{-1} . In fact, neither the kinetic coupling term nor the He-He interaction are able to couple vibrations of the inner well with those of the outer one. For the systems involving He₂^{*-}, at $J = 0$, and for even values of the inversion parity, the exchange of He atoms, and the permutation of nuclei inside the anion dimer, energy convergence was achieved to within 10^{-2} cm^{-1} by using six vibrational functions, even L values up to 15, and sixteen ℓ_i , ($i = 1, 2$),

values, *i.e.* $0 \leq \ell_i \leq 15$.

4.1. Complexes involving He^{*-}

Figure 3 displays angular and radial distributions for the ground state of the $\text{He}_2\text{-He}^{*-}$ complex. The $\nu = 0, 1$, and 2 states of the He-anion dimer were considered as the vibrational basis set. The distribution on R_1 (or R_2), the He- He^{*-} distance, is essentially the same that the $\nu = 0$ state of the dimer, and its energy, $-32,165 \text{ cm}^{-1}$, is almost twice that of the $\nu = 0$ level, see Table 1. The angular distribution presents a clear maximum at $\cos\gamma = -1$, *i.e.* with the He atoms at opposite sides of the anion, and the distance between them, R_{12} , peaks at two times the maximum of the R_i distribution, showing a preference of the complex to be in a linear He- He^{*-} -He arrangement, which is a clear signal of solvation. When one considers additional He atoms, it is clear then that by accounting for the two other possible orthogonal directions the placing of ~ 6 He atoms around the anion forming a bi-pyramid (tetrahedron) is a probable arrangement, as long as the He-He distances are not too short and the corresponding interaction is not excessively repulsive.

Taking as a basis the $\nu = 0, 13$ and 14 states of the dimer, Figure 4 depicts the radial distribution on R_i and the angular distribution of an excited state with an energy of $-16,231 \text{ cm}^{-1}$. The radial distribution mainly corresponds to a He atom pretty close to the anion ($\nu = 0$) while the other He atom is in the $\nu = 13$ state, *i.e.*, sustained by the secondary well (and viceversa, due to their boson character). The angular distribution, in turn, is almost isotropic with values near 0.5 all along the angular variable. Since $J = 0$, the emerging picture is that of a He atom rotating around the anion at a distance of $\sim 1 \text{ \AA}$, while the other describes in the opposite sense a wide annulus. A similar situation is presented in Figure 5 for a state of $-16,185 \text{ cm}^{-1}$ of energy, as refers the radial distribution. However, the angular distribution presents two nodes and maxima at $\cos\gamma = 0, \pi/2$ and π , *i.e.*, it corresponds to a bending excitation.

Using $\nu = 12$, the last state supported by the inner well of the He-anion interaction, together with $\nu = 13$ and 14, Figure 6 displays again radial and angular distributions corresponding to an excited state of -77.0 cm^{-1} of energy. It presents the nodal structure of the $\nu = 12$ state and the

signature of a bending excitation. Note that in the last three figures, the radial distributions are clearly separated by the barrier, and the two He atoms are unable of tunneling through it.

Figure 7 shows a comparison of the effective potential modeling the He-He₇^{*-} interaction and the region of the outer shallow He-He^{*-} interaction. Each of them supports two bound states, which are also shown. Although the potentials are very close, the mass effect of the bipyramid anionic partner lowers the corresponding energies from -1.2657 cm⁻¹ ($\nu = 13$) and -0.0054 cm⁻¹ ($\nu = 14$) of the He-He^{*-} complex to -2.0018 cm⁻¹ ($\nu = 0$) and -0.1619 cm⁻¹ ($\nu = 1$), respectively. Consequently, the corresponding wave-functions are much more localized for the He-bypiramid model system than for the He-He^{*-} one. Using those $\nu = 0$, and 1 as vibrational basis set, with the rest of quantum numbers identical to the used on He₂-He₂^{*-}, the different distributions of the ground state of He₂-He₇^{*-} are depicted in Figure 8. The energy of -3.983 cm⁻¹ is almost two times that of the ground state of He-He₇^{*-}, and thus the distribution on R_i is the same than its $\nu = 0$ state. In turn, the He-He distribution, and in spite of presenting its peak near two times the maximum of the previous one, is very broad and extends from ~ 1 Å up to ~ 21 Å. The angular distribution is almost isotropic in the range of γ from π to $\pi/2$, and quickly decreases going to linear arrangements. So, we can not see the signature of solvation within this model which leads to energies and conformations compatible with the PIMC results. Indeed, the PIMC findings²² do not achieve such solvation but the formation of a deep dimple on the surface of the helium cluster.

We are aware that heavier anionic species as He₇^{*-} have not been detected by time-of-flight mass spectrometry. However, in case that such species form, it is also possible that the lack of detection is due to their worse relation of mass and lifetime as compared with the lighter species. In fact, the arrival time to the detector could be longer than the lifetime of the anion, i. e., it would disappear during its travelling. By simply equating the electric force and the Newton law, one realizes that the flight time scales as the square root of the mass. So, for a given electric field, if He^{*-} spends 3.3 μ s to travel 1 m, He₂^{*-} would spend 4.6 μ s,¹² and He₇^{*-} would spend 8.7 μ s. Now, the lifetime τ for detachment of He^{*-} is ~ 359 μ s,⁶ while it reaches ~ 135 μ s for He₂^{*-},⁹ i. e. a factor larger than 2.5. By fitting this superlinear behavior to an exponential law in terms of the size

N of the anion, $\tau(N) = Ae^{-Bf(N)}$, one estimates a lifetime for He_7^{*-} of $\sim 7.4 \mu\text{s}$ ($f(N) = \sqrt{N}$; $\sim 1 \mu\text{s}$ if $f(N) = N$ is assumed), that is smaller than its above mentioned time of flight. Since the latter also scales with the inverse of the square root of the electric field, this should be correspondingly increased in order to get some signal. For instance, to decrease the flight time of He_7^{*-} from $8.7 \mu\text{s}$ to $5 \mu\text{s}$, the electric field should be increased from the value used of 50 V/cm^{12} to 150 V/cm .

4.2. Complexes involving He_2^{*-}

The anisotropic He-He_2^{*-} system presents one bound level at each orientation in the whole range $[0 - \pi/2]$, the energies going from $\sim 0.46 \text{ cm}^{-1}$ in the collinear arrangement to $\sim 2 \times 10^{-4} \text{ cm}^{-1}$ at the perpendicular orientation $\theta = \pi/2$. Radial distributions of these states at selected orientations (0 , 45 and 90 degrees), see Figure 2, labeled according to their energies, are displayed in Figure 9. They exhibit a high degree of delocalization. Their square-root are the $\phi_0(R; \theta_n)$ functions of Eq. (9) which, after orthogonalization, serve as vibrational basis set to study the tetra-atomic $\text{He}_2\text{-He}_2^{*-}$ system. The 2D ground level is estimated through a typical calculation in Jacobi coordinates³⁸ its energy being of $E_{00} = \sim -0.23 \text{ cm}^{-1}$. The corresponding radial distribution is also depicted in Figure 9, and extends over an ample region from $\sim 10 \text{ \AA}$ to $\sim 45 \text{ \AA}$.

Radial and angular distributions for the ground level ($E = \sim -0.46 \text{ cm}^{-1}$) of the $\text{He}_2\text{-He}_2^{*-}$ complex are shown in Figure 10. The distribution in R , the He-center of mass of anion distance, whatever be the helium atom, is the same than the triatomic one already mentioned in the precedent paragraph. The distribution in $\cos\theta$ is isotropic with a extremely weak preference for colinear arrangements, while the distribution in $\cos\gamma$ remains almost isotropic from π to $5\pi/12$ and then goes to zero for smaller angles. The He-He distance, in turn, presents a maximum at almost two times the peak in R , although is also spreaded on a wide range from $\sim 20 \text{ \AA}$ to beyond $80 \text{ \AA}$. In this situation is difficult to predict what is going on when one considers the presence of additional He atoms. In this regard, some insight can be obtained by applying the simple model outlined at the end of subsection 3.2.. In Figure 11 we show the evolution with the size N of the radial distributions corresponding to the ground states of $\text{He}_N\text{-He}^{*-}$ complexes obtained by using the

effective Hamiltonian of Eq. (10). For $N = 3$ ($E \sim -0.70 \text{ cm}^{-1}$), the R distribution is the same and the R_{12} one is very similar to those corresponding to $N = 2$ already shown in Figure 10. For $N = 4$ ($E \sim -1.70 \text{ cm}^{-1}$), there is a dramatical change: the R distribution is picked at $\sim 17 \text{ \AA}$, while R_{12} does at $\sim 8 \text{ \AA}$, almost one half of the R peak, pointing towards the packing of the He atoms while the dimer anion is placed far away, so confirming the heliophobic character of the He_2^{*-} anion. These results, with regards to their binding energies and distributions, are in line with the PIMC findings.²²

5. Conclusions

We have studied small complexes of helium atoms and anionic species He^{*-} and He_2^{*-} , the latter being considered as a rigid rotor. The study of $\text{He}-\text{He}^{*-}$ constitutes a first step that allows the characterization of $\text{He}_2-\text{He}^{*-}$ complexes. To this end, a simple model of additive pair-wise potentials has been used. The ground level of this system already announces a full solvation of the impurity, which is achieved according with previous PIMC calculations for six He atoms surrounding the anion forming a bipyramid. A simplified model for dealing with the $\text{He}_2-\text{He}_7^{*-}$ system is unable, however, to elucidate the further solvation of this bipyramid. As regards the possible detection of these kind of heavier metastable anion species in time-of-flight experiments, which have not been observed yet, a reasonable increase of the electric field is suggested in order to decrease the corresponding flight time, reaching values below the envisaged lifetimes.

In turn, $\text{He}_N-\text{He}_2^{*-}$ complexes are accurately studied for $N \leq 2$ and, in an approximate way, for $3 \leq N \leq 4$ by resorting to the use of an effective Hamiltonian. These studies show clearly the heliophobic character of this dimer anion.

Finally, it is evident that for the He_3^- system, the two potential models lead to different results depending on the assumed core, atomic He^{*-} or molecular He_2^{*-} one. For matching both kind of model systems, this triatomic anion could serve as a prototype to determine the possible existence of isomers and, that is more important, to refine the pair-wise potential model involving the $\text{He}-$

He^{*-} interaction. This could be achieved by relaxing the He₂^{*-} bond length, which at present is fixed at its equilibrium value, and carrying out additional electronic structure calculations on the He-He₂^{*-} system. Work in this direction is in progress.

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FIGURES

Figure 1: Potential energy for He–He^{*−} obtained by splines fitting to the *ab initio* points of Ref.¹⁷ The inset amplifies the region of the secondary well. See text for details.

Figure 2: Potential energy for the $\text{He}-\text{He}_2^*$ interaction for different values of the θ angle between the vectors $\mathbf{r}$ and $\mathbf{R}$, see text. Points are *ab initio* results from Ref. ¹⁷ and lines correspond to the fit by means of Eq. (1).

Figure 3: He₂–He^{*−} system. Angular (cosγ) distribution (blue line, upper x axis-right y axis), and radial distributions (usual xy axis; red line: R₁ or R₂, the He–He^{*−} distances, green line: R₁₂, the He–He distance) for the ground state with a binding energy of 32,165 cm^{−1}, see text.

Figure 4: An excited state of the $\text{He}_2\text{-He}^{*-}$ system at an energy of $-16,231\text{ cm}^{-1}$ showing the main contribution of the $\nu = 0$ and $\nu = 13$ levels of the He-He^{*-} interaction through the radial distribution on the R_1 or R_2 distances (usual xy axis). The angular distribution (upper x axis-right y axis) is almost isotropic.

Figure 5: An excited state of the $\text{He}_2\text{-He}^{*-}$ system at an energy of $-16,185\text{ cm}^{-1}$ with radial distribution on the R_1 or R_2 distances (usual xy axis) identical to the precedent state of Figure 4. The angular distribution (upper x axis-right y axis), in turn, shows two nodes, and maxima at 0 , $\pi/2$, and π , *i.e.* it corresponds to a bending excitation.

Figure 6: A highly excited state of $\text{He}_2\text{-He}^{*-}$, $E=-77.005\text{ cm}^{-1}$, mainly corresponding to the combination of $\nu = 12$ and $\nu = 13$ levels of the He-He^{*-} interaction. The angular distribution also describes a bending excitation.

Figure 7: On the usual xy axis, comparison of He–He₇^{*−} model interaction (red line) and the region of the outer shallow He–He^{*−} interaction (blue line), together with the couple of states (x-right y axis) supported by each of them. The same colors have been used for the states and the potentials, using solid lines for the ground levels and dashed lines for the excited ones, and have been placed with respect to their corresponding energies.

Figure 8: Radial (usual xy axis) and angular (upper x axis-right y axis) distributions for the ground state of $\text{He}_2\text{-He}_7^{*-}$ model system. The energy is of -3.9831 cm^{-1} .

Figure 9: Distributions of the ground vibrational He–He₂^{*-} states at selected orientations of the corresponding interaction, see Figure 2, labeled according to their energies, and radial distribution (black line) of the triatomic ground level. Their square-root form part of the {g_n} basis set, see text, to study the tetra-atomic He₂–He₂^{*-} system.

Figure 10: Radial (usual xy axis) and angular (upper x axis-right y axis) distributions for the ground state of the $\text{He}_2\text{--}(\text{He}_2^{*-})\text{--He}$ complex.

Figure 11: Evolution with the size N of the radial distributions corresponding to the ground states of $\text{He}_N\text{--He}_2^{*-}$ complexes according to the tetra-atomic effective model, see text. Solid lines: He–c.m. anion distance; dashed lines: He–He distance. Red: $N = 2$; green: $N = 3$; blue: $N = 4$.

Graphical TOC Entry

Probability density distributions of the ground vibrational state of the $\text{He}_2\text{-He}_7^*$ system.