

A quantum chemical approach towards the electronically excited states of helium clusters

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Abstract. We have investigated the electronic energies of the ground and excited states of an octahedral helium cluster by quantum chemical ab initio calculations. The excited levels were calculated for the central atom for a set of different inter atomic separations. Our approach yields potential energy curves which are suited to describe a density dependence of the spectral features as previously observed in photo excitation experiments. The potential energy curves of the $2s$ and $2p$ states show a hump at $R \cong 2.5 \text{ \AA}$ caused by the strong perturbation of neighbouring atoms. The existence of this hump explains the experimentally observed blue shift and its dependence on the cluster size or density, respectively. The potential curves of the higher levels show almost constant energies. Perturbations of these levels are small, because the overlap between the Rydberg orbital and the orbitals of the surrounding atoms is small. This is the case for both small R values where the Rydberg orbital is well outside the cluster as well as for large R where the density drastically decreases. These findings coincide with the un-shifted features of small clusters observed in experiments.

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1 Introduction

The question of how electronic states evolve from the atom towards the bulk has remained a challenge in chemical physics until the present day. Helium clusters are interesting model systems to investigate such changes, because of their simple electronic ground state. A remarkable feature of He clusters is that the number density can be varied over four orders of magnitude by changing the cluster size and isotopic composition. With only two electrons per atoms He is the element of choice for calculating many body systems with ab initio methods. Previous experimental work on the excited states of clusters of He has revealed significant differences when compared to heavy rare gases [1]. While their excitations are well described by the concept of Frenkel and Wannier excitons [2–4] as well as by confined and perturbed higher lying excited wavefunctions [5–7], the excited states of He clusters behave like perturbed excited atoms [8]. Recently, Rydberg states have been observed in pure He clusters and nanodroplets [9]. The clusters were investigated by monochromatic synchrotron light and energy and time resolved fluorescence spectroscopy in different wavelength regions. The analysis of the spectral features revealed four different types

of Rydberg states in He clusters. (i) Rydberg electrons, which orbit around small ($N < 100$) positively charged He clusters. (ii) Single excited Rydberg He atoms at the surface of large He droplets. (iii) He excimers in bubbles inside very large He droplets [10]. Further analyses showed that in ^3He droplets the bubbles travel randomly towards the surface in accordance with their anticipated non-superfluid state. For the superfluid ^4He droplets an average speed of the bubbles of 7 m/s, well below Landau's critical velocity of 58 m/s [2] could be derived. (iv) Excited He nanodroplets eject He excimers and atoms in Rydberg states up to $n = 11$ from their surface on a timescale much shorter than the radiative lifetime [9, 11].

The present paper deals with the excitation spectrum of He clusters and their dependence on the number density. The spectrum of small He clusters ($N < 100$) shows a Rydberg series of highly resolved sharp lines up to $n = 9$ converging towards the ionisation limit [9]. The lines with lower quantum numbers show blue shifted wings. Those wings have been explained by the unfavourable overlap of the excited electron and the $1s^2$ ground state of the surrounding atoms in the cluster according to the Pauli principle [9]. In a small cluster this repulsion will cause an extended electronic wavefunction to remain outside the cluster. An excited electron will therefore reveal lower

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binding energies and its orbital will thus be more extended. Clearly, this tendency of electrons to avoid entering the He cluster core will control the spectral features which therefore will depend on the principal quantum number n and the cluster size N . For lower n the electronic wavefunctions will have a much larger overlap with the small cluster and therefore will be more strongly perturbed than for highly excited states. This somewhat hand waving argument has been used in previous work [9] in order to interpret the fluorescence excitation spectrum of small ($N < 100$) He clusters. As an approximation the Bohr radii (r_n) for hydrogen were employed. Although this previous work could elucidate the general trends, more thorough methods are needed to quantitatively explain the underlying physics.

In this work we will report on high level ab initio calculations on a He₇ model cluster. The central He atom of the cluster is octahedrally surrounded by six further He atoms. For this cluster we investigate the energies of core excited states. By variation of the He-He distance we simulate different densities of the experimental cluster. A highly symmetric geometry is not a realistic description of liquid He clusters in their ground state, but an octahedron is a good model system to simulate different densities of the cluster, which in experiments have been found to influence the excitation energies [8]. An octahedral symmetry has also been chosen because in the bulk, He is found to have 6 nearest neighbours on average [12]. Excitations of the central He atom represent the fully coordinated interior atoms in nanodroplets. We presume, that the symmetry plays a minor role since the average interatomic separation is the significant parameter. A fully realistic model which accounts for the liquid nature would involve ground and excited state calculations for multiple sets of ground state geometries and averaging over the energies. Such calculations would go far beyond our present work and have yet, to the best of our knowledge, not been performed.

In this paper we will address the problem of the electronically excited states of He clusters using state of the art quantum chemical methods. Our approach considers Rydberg states as well as valence excitations. We will present potential energy curves that quantitatively explain the experimentally observed shifts and their density dependence.

2 Methods

The calculations reported in the present study were carried using the Bochum suite of wave function based quantum chemical ab initio programs [13–16]. Electronic wave functions for the ground state as well as for the ionised state were calculated by the Hartree-Fock self consistent field method (SCF). The orbitals had to be localised by a Foster-Boys localisation in order to ionise and excite the central He atom. However, the accuracy for ionisation and excitation energies which can be obtained at the Hartree Fock level is not sufficient. Therefore, dynamic correlation effects were taken into account for both the ground and the ionised state by the multi-configuration coupled electron

pair approximation (MCCEPA) [16] which is an approximation to the multi-reference coupled cluster method. For valence excitations we performed state averaged complete active space SCF calculations (CASSCF) and MCCEPA calculations, while higher Rydberg states were treated within the frozen core approximation [17, 18]. In the frozen core approximation it is assumed that the Rydberg electrons in higher Rydberg states do not change the form of the occupied orbitals of the ion. Therefore, one only has to determine the form of the virtual orbitals in the field of the ion. The Rydberg orbitals are hydrogen-like and characterised by an effective quantum number which describes the energy difference between the frozen core states and ideal hydrogen-like states. In all calculations we used the 10s basis set of Huzinaga [19] contracted to 6s and extended by $p(2.0,0.7,0.2)$ and $d(1.4,0.4)$ polarisation functions and semi diffuse $s(0.03)$ and $p(0.07)$ functions. For the He at which the core excitation took place it was necessary to use the uncontracted 10s basis set to allow for changes in the orbital shape of the 1s orbital. Furthermore, a Rydberg basis of Kaufmann et al. [20] which was able to describe Rydberg states up to $n = 5$ was added at this atom.

3 Results and discussion

The energies of the different electronic states of the He₇ cluster were obtained by the following procedure. First, the ground state energy was calculated at the Hartree-Fock level. Next, the orbitals were localised and the ground state energy was obtained at the MCCEPA level. In the last step the energies were corrected for the basis set superposition error (BSSE) by a counterpoise correction as proposed by Boys and Bernardi [21]. Even for the shortest distance of 2 Å the BSSE correction is only 3.3 meV for the entire cluster. This is negligible for the excitation energies but important for a reliable description of the weak van der Waals interaction in the ground state. The potential energy curve of the ground state is shown in Figure 1. The curve is very similar to that of the He pair potential having a shallow well with a minimum of –6 meV at 3 Å and strong repulsion at smaller internuclear distances.

The energies of the excited states with $n \geq 3$ were calculated as follows. In a first step a SCF and MCCEPA calculation for a locally ionised state was performed. The ionisation potential obtained in this fashion is increased compared to the Hartree-Fock level. It is well known that this energy change stems mainly from the loss of the intra pair 1s correlation energy, which is about 1 eV in the ground state of a He atom. The orbitals of the excited states were then obtained within the frozen core approximation. For the higher Rydberg states ($n = 3$ and higher) the interaction of the Rydberg electron with the core orbitals is only small. Therefore, it is sufficient to correct the excitation energies at the frozen core level by the intra pair correlation energy of the ground state orbital which is ionised. The inter pair contributions between the Rydberg electron and the cluster electrons to the dynamic correlation are neglected. Jungen and Staemmler [22] analysed

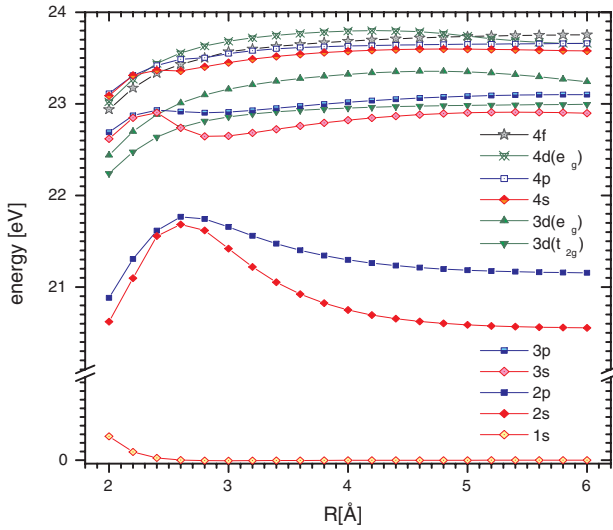


Fig. 1. (Color online) Vertical excitation energy curves of the lower Rydberg states of an octahedron of 7 He atoms. The energy E refers to the absolute energy of the cluster at a specific internuclear distance R . The $4d(t_{2g})$, and four of the $4f$ components are not shown since they have similar energies to $4p$. Only singlet curves are shown.

these contributions for different Rydberg states in LiHe and found distant-dependent pair energies which were always smaller than 0.04 eV for $n = 3$ states and smaller than 0.02 eV for $n = 4$ states. All energies are given as relative energies with respect to seven He atoms. Figure 1 shows the resulting energies for a set of internuclear distances ranging from 2 to 6 Å. Only singlet states are shown since optical transitions from the singlet ground state into triplet excited states are forbidden. At large distances the energies are close to the He atomic levels. The frozen core approximation does not necessarily yield states which are orthogonal to the ground states. This affects notably the s states, which are usually too low in energy. When calculating the energies for an isolated He atom we obtained a $3s$ energy which is 0.14 eV lower than the spectroscopic value, while the energy of the $3p$ state deviated by only 0.03 eV from the spectroscopic value. For the same reason as well as because of increasing significance of correlation effects the frozen core approximation is not valid for the $2s$ or $2p$ states. Therefore, we obtained the $2s$ and $2p$ orbitals by a state average CASSCF calculation. Dynamic correlation was considered by MCCEPA calculations for the individual states. For internuclear separations R larger than 5 Å the deviation of the energies of the $2s$ and $2p$ states from the atomic levels is smaller than -63 meV. The resulting potential curves are shown in Figure 1.

The $2s$ and $2p$ states are characterised by orbitals which are of a size similar to or smaller to the internuclear distance of our model cluster, as well as of bulk liquid He. For internuclear distances between 3 and 6 Å the radius of the $2s$ and $2p$ orbitals varies only slightly between 2.6–3 Å while it increases quickly to 5 Å for smaller distances. Therefore, relatively large perturbation effects are expected. Indeed, both the $2s$ and the $2p$ potential curves

rise in energy for distances smaller than 4 Å and reach a maximum of 21.68 eV and 21.76 eV, respectively, at 2.5 Å. The increase in energy is attributed to the repulsion between the excited electron and the neighbouring ground state orbitals. For smaller internuclear distances the levels decrease rapidly because the excited state wavefunction lies outside the model cluster. For this situation the wavefunction has strong Rydberg character and the cluster gains several eV in binding energy. The regime of small internuclear distances is particularly important for relaxation processes after electronic excitation and will be discussed in a forthcoming paper.

The $n \geq 3$ states have radii $\langle r \rangle$ well outside the cluster, where $\langle r \rangle = \sqrt{\langle r^2 \rangle}$ denotes the extension of the Rydberg orbital. Within our investigated range of internuclear separations the Rydberg wavefunctions lie between 5.7 and 9.7 Å for the $n = 3$ states and 5.7 to 17 Å for $n = 4$. Figure 1 shows for all potential curves almost constant energies for internuclear distances $R > 3$ Å. At smaller internuclear separations the energy decreases rapidly similar to the $2s$ and $2p$ states, because strong ionic-like bonds are formed [23]. At large internuclear distances weak interactions of the higher Rydberg orbitals with the surrounding He atoms can be observed, e.g. the d -states are split by ligand field splitting into a t_{2g} state and an e_g state. As expected the e_g state is more repulsive. Humps, similar to the $2s$ and $2p$ states are not observed. In the range of $R > 3$ Å the overall energy variations are smaller than 0.2 eV. The energy is slightly lower when the interatomic separation matches a node of the Rydberg orbital and is increased when it matches a loop [22]. Curve crossings because of the inner loops of the $3s$ and $4s$ orbitals can be observed at $R = 2.5$ Å.

The artificial He₇ cluster investigated here represents a lower limit for the relevant size range in experiments but it nevertheless allows conclusions for much larger sizes or even the bulk. One of the main characteristics of He clusters which has to be considered in this discussion is their strongly varying density with size. The average distance between He atoms in the centre of large ⁴He clusters, as well as in bulk liquid ⁴He, is 3.58 Å. Towards the surface of clusters this value increases smoothly. As a consequence, He clusters can be regarded as disordered systems displaying a wide range of bond lengths. Depending on the size of the clusters the average bond length varies, because small clusters have more surface contributions [8]. Optical excitations can be understood as Frank-Condon-type transitions taking place at a wide range of internuclear separations, because of the large amplitude of the zero point motion. If, for instance, a cluster having a mean internuclear separation of 3.6 Å is considered, vertical transitions will happen at R values from 2 Å to 5 Å. However, excitations at extreme distances contribute to a much lesser extent to the spectrum than those at 3.6 Å. Eventually, the shape of the excitation spectrum will depend on the R dependence of the energy difference between the excited state and the ground state. Real ⁴He₇ clusters have an average internuclear separation of ~ 5 Å in the ground state [24]. At $R = 5$ Å the potential curves of the $2s$ and

$2p$ states are almost unchanged from the free atom levels. The excitation spectrum will therefore be dominated by a sharp line at the atomic resonance energy. The zero point motion will nevertheless cause a small fraction of excitations to happen at distances where the $2s$ and $2p$ potential curves rise. This small fraction of excitations will appear as a blue shifted wing in the spectrum, which indeed is observed in experiments.

The situation differs drastically for large nanodroplets with $N = 10^4$. These have on average an internuclear separation of $R = 3.6 \text{ \AA}$ similar to bulk liquid He. Consequently, excitations into the $2s$ and $2p$ states will be controlled by the humps in the potential curves. 3.6 \AA is close to the turning point of the potential energy curves. The wide range of excitations taking place from $R = 2 \text{ \AA}$ to $R = 5 \text{ \AA}$ lead to an almost symmetric feature with a width in the order of the height of the hump. Such features are indeed observed in experiments with large He clusters for both the $2s$ and $2p$ states.

We note that the height of the humps of the $2s$ and $2p$ states agrees fairly well with the magnitudes of the shifts observed experimentally. The spectrum of large clusters is dominated by broad features, which extend to 22.1 eV and 22.4 eV for ^3He and ^4He , respectively, and a gap to the $n = 3$ levels. The shift of the $2s$ band is indeed found to be larger than for the $2p$ band which coincides with the steeper slope and greater height of the $2s$ potential curve. According to the comparatively small size of the $2s$ and $2p$ orbitals we presume that the shape of the potential energy curves of the $2s$ and $2p$ states will not significantly change if one or more outer shells will be included into the calculation. We note further, that the experimentally observed difference in shifts between ^3He and ^4He clusters are consistently explained by their different number density, i.e. internuclear separation [8]¹.

The potential curves of the higher levels with $n > 3$ do not change much in energy over the relevant range of R between 2.5 and 6 \AA . This behaviour agrees well with what is observed in experiment. The spectrum of small ^4He clusters with $N < 30$ consists in the high n region of sharp lines only, which indicate that perturbation is small. This observation is explained by the Rydberg character of these levels. For small R values the Rydberg electron is well outside the cluster and there is only marginal overlap with the ground state He atoms. For large R the cluster radius becomes similar to the radius of the electronic wavefunction values, but the density is too low to produce enough overlap for noticeable perturbation. In this regime the He cluster behaves more like a dense gas. The broad bands for $n \geq 3$ in large clusters cannot be explained by the present small model cluster. More He shells have to be taken into account.

Lifetime effects may contribute significantly to the shape of the spectrum. The concept of individual electronic excitations in the cluster allows, for instance, for excitation transfer among the atoms. This effect will scale with the overlap of the excited wavefunction with the ground state of one of the neighbours and thus depend

on the number density inside the cluster and on the principal quantum number n . The experimentally observed $2s$ and $2p$ bands of large clusters are indeed broad and may include contributions from a short electronic lifetime.

In conclusion we have investigated the levels of small He clusters by quantum chemical ab initio calculations. The resulting potential energy curves of the $2s$ and $2p$ states show that for realistic densities of small clusters the atomic energies remain almost unaffected, because the $2s$ and $2p$ orbitals are significantly smaller than the internuclear separation. For the artificial situation of small internuclear distances the states are characterised by large humps. These humps become important for the much denser nanodroplets and explain the experimentally observed large blue shifts of the $2s$ and $2p$ states. Higher states remain unaffected over the entire relevant range of densities which agrees well with the experimental observation for small clusters. However, more He shells have to be included in order to simulate the states with higher quantum numbers of large clusters.

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¹ $R(\text{bulk liquid } ^3\text{He}) = 3.95 \text{ \AA}$, $R(\text{bulk liquid } ^4\text{He}) = 3.58 \text{ \AA}$.