



# A simple model for a theoretical study of the spectral line shifts of alkali atoms attached to helium nanodroplets



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## ABSTRACT

The lowest  $s \rightarrow s$  line shifts of the alkali atoms Li and Na attached to  $^4\text{He}$  nanodroplets have been estimated using *ab initio* quantum chemical methods with a physically viable cluster model of alkali atom (Li/Na) on the surface of helium atoms. First, detailed non-relativistic calculations are made using size extensive Configuration Interaction (CIS(D)) yielding the line shift of the  $2s \rightarrow 3s$  and  $3s \rightarrow 4s$  transitions of Li and Na in good agreement with available experimental results. Next, relativistic density functional calculations were performed yielding consistent results for the line shifts compared to the non-relativistic estimates and in good agreement with experimental results.

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## 1. Introduction

Spectroscopic properties of atoms and molecules embedded in superfluid He [1,2] have been extensively investigated both experimentally and by various theoretical methodologies [3,4]. Embedded system inside liquid He creates a cavity or bubble-like structure due to the strong Pauli repulsion. The shape and size of the bubble are determined by the nature of the impurity and the angular momentum of the electrons [3]. The bubble size increases when the system goes over to its excited states [5,6] and depends on the external pressure [7–10]. Studies on such embedded systems not only yield the spectral changes induced by the embedding system but also furnish various information about the superfluid itself [3]. In recent years such studies using ultracold ( $\sim 0.4\text{K}$ ) He nanodroplets opened up vast avenues in matrix isolation spectroscopy in which the high resolution electronic spectra of a number of foreign species attached to such droplets could be analysed [11–13]. The effectiveness of the spectra of such dopants to serve as a spectroscopic probe to investigate the properties of nano quantum clusters [14,15] started with the first experimental observation of the attachment of foreign atoms in He nanodroplets [16]. The nanodroplets are readily formed using different experimental techniques including gas jet expansion [11]. Attachment of different species, in particular the alkali atoms, occurs in the

course of passage of the droplets through vapours of the species. A large number of such dopants attached to He nanodroplets are currently available for spectroscopic observations [11]. In general, many atoms and molecules are solvated by He droplets [17] and bulk properties of the nanodroplets give detailed understanding of the superfluidity at the microscopic level [11]. Quantum chemical calculations based on density functional approach [18] or many-body Hartree/Hartree–Fock method [19–21] have been performed on molecules solvated in helium nanodroplets to study structural properties of dopant molecules as well as to simulate their rovibrational Raman spectra. The Hartree approach was used with an interesting partition of the dopant and the He system [21]. However, several atomic systems particularly, the alkali atoms do not solvate inside the droplet, instead they reside on the surface [22]. The surface region of the He nanodroplets behaves differently basically due to reduced symmetry, lower density and surface fluctuations. In this context alkali atoms are particularly important, as they are weakly bound to He droplets [23,24] and reside above a dimple on the surface of the droplets, thereby rendering analysis of the surface properties with such external microprobes [25]. Study of the spectral properties of alkali atoms are easier due to their simple structure and hence details of such spectroscopy in attachment with He droplets are useful for investigating their surface regions [25–29]. Most of the studies involving alkali atoms attached to He nanodroplets are limited to their first dipole allowed excited states [17,25,30–32]. Only very recently investigations on higher excited states involving different symmetries have been reported [17,33,34]. The general observations related to the spectra of the dopant atoms from these studies are the spectral line shifts of the

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atoms with respect to the free systems, asymmetric and substantial change in the spectral line profiles. Further, it was observed that for most of the alkali dopants desorption occurs within picoseconds after excitations [17,23,24,27,34], resulting in either bare atoms or alkali–He exciplexes depending on the excitation frequency of radiation. Analysing the positions of the alkali atom spectral lines attached to He nanodroplets of different sizes typically ( $\sim 1000$  to several thousands) it was found that for the dipole allowed lowest  $s \rightarrow p$  transitions, the shifts are rather small [17,30–32,34] but the line profiles change appreciably. In this regard, important investigations have been performed by Loginov et al. [17] and by Hernando et al. [34] for the spectral line profiles and shifts for the lowest  $s \rightarrow s$  transitions in Na and Li attached to such droplets as well as dynamics of the problem. Appreciable shifts of such lines compared to the free atomic line positions have been observed. It was further observed that the shift depends on the size of the nanodroplet and increases slightly [17] with its increase. Essentially  $s \rightarrow s$  transitions occur due to the reduced symmetry of the surface structure after attachment. Theoretical investigations on the spectral characteristics use mostly the alkali–He droplet interaction potential as a sum of individual alkali–He pair potentials, the sum being extended over the He atoms constituting the droplet [23,25,34]. Continuous density functional approach used to represent the density of the He droplet ensures the sum to be replaced by an appropriate integral. An alternative method is based on a perturbative treatment of the valence electron, the positive core of the alkali and the He droplet, the last being treated by density functional approach. This method takes care of He induced mixing of electron configurations of alkali atom [22]. These approaches are very successful in predicting the overall spectral characteristics compared to experimental observations. The line shifts are, however, not so well predicted as the profiles [17,34].

In this Letter we consider a simple but novel approach to obtain the spectral line shifts of atoms attached to  $^4\text{He}$  nanodroplet, in particular for the  $2s \rightarrow 3s$  transition in Li and  $3s \rightarrow 4s$  transition in Na. The method is similar to the cluster model for foreign atoms embedded in bulk liquid He for estimating the line shifts and profiles. Its efficacy for alkali and alkaline earth atoms embedded in such liquid matrix [35–41] has been well established. Due to the nature of the attachment of the alkali atom on the surface of He nanodroplet, the model structure proposed is different from that used for bulk structure. This is being done in a judicious way as described in Section 2.

## 2. Methodology

Our aim is to theoretically obtain the spectral line shifts associated with the low-lying transitions in Li and Na attached to He nanodroplets, where experimental observations are available. The method we propose is general and can be applied for cases irrespective of the polarity of the transition. However, currently we would consider the transitions where the experimental estimates for the line shifts are appreciable so that the results of our calculation could be compared without ambiguity, representing a good test of the proposed model and methodology. In this respect we have chosen the  $2s \rightarrow 3s$  transition of Li and  $3s \rightarrow 4s$  transition in Na attached to He nanodroplets [17,34]. The associated experimental spectral profiles show substantial change of the line profiles and shift of the peak positions compared to their free states. The  $s \rightarrow s$  transitions in both Li and Na are dipole forbidden in the free systems but due to symmetry lowering when located at the surface of liquid He droplets, the transitions become allowed, albeit with relatively low but measurable intensity. In the case of Li two isotopes was used [34]. In  $^6\text{Li}$  the experimental blue shift is slightly less than in the case of  $^7\text{Li}$ . In the case of Na the shift is seen to be

dependent on the number of He atoms. For cluster sizes ranging from  $\sim 2000$  to  $20\,000$  He atoms Loginov et al. [17] observed that the shifts varied from  $570\text{ cm}^{-1}$  to  $720\text{ cm}^{-1}$ . Hernando et al. [34] considered the case of  $1700$  He atoms and obtained experimentally the spectral blue shift of  $570\text{ cm}^{-1}$  with a width of  $400\text{ cm}^{-1}$ . In the same paper they also considered theoretical studies with  $1000$  He atoms and obtained the calculated values of  $350\text{ cm}^{-1}$  for the shift and  $370\text{ cm}^{-1}$  for the width. However, for Li–He cluster, Hernando et al. [34] did not specify the numerical value of the shift but an estimate of  $\sim 300\text{ cm}^{-1}$  of the same can be obtained from Fig. 4 of the same paper [34] compared to their experimental value slightly greater than  $600\text{ cm}^{-1}$ . The calculations made in this present Letter do not consider the nuclear mass effect. In comparing our theoretical results that are made with the simplified model including only a small number of He atoms we will consider as a reference that the experimental value of the shift of Li as well as that of Na close to  $600\text{ cm}^{-1}$ .

Our model of attachment rests on simple arguments based on the fact that the potential between alkali and He atoms is very weak mostly due to van der Waals interaction. Due to the rapid reduction of the strength of the potential between the alkali atom and He with distance, the interaction term is dominated mostly by the nearest neighbour He atoms. The subsequent He atoms give only a minor correction to the main interaction potential. Unlike alkali atoms in bulk liquid He, in which we have an essentially spherically symmetric structure of the He surrounding, here the interaction with the alkali atom is largely asymmetric in nature. At sufficiently large distance from the droplet the approaching alkali atom will see a surface of He atoms belonging to the droplet. On close encounter it will always find a He atom directly beneath and will try to push it downwards in such a way that at equilibrium the distance between the alkali atom and all other neighbouring He atoms at the surface and also that which is pushed below the surface are equal. Thus in equilibrium we have a bi-conical structure, in which in one vertex is sitting the alkali atom and in the other vertex we have a He atom. The distances of the He atom at the second vertex below the base ring from those in the ring are assumed the same. However due to surface fluctuations the distance between the neighbouring He atoms at the ring is not the same as the distance between the vertex He atom and those in the ring. This can be calculated in our static model from the alkali–He distance and the distance of the vertex He to ring He by using a simple geometrical model giving the radius of the base ring thereby generating the number of equally spaced He atoms along the circumference of the ring. Since He–He interaction is relatively less important compared to that of the alkali He interaction in producing the shift in the alkali spectra, this factor is not so crucial in this calculation. This also alleviates having to deal with the very weak and difficult He–He interaction. A simple symmetry argument shows that at most five He atoms can be placed in the ring in which the vertex having the He atom is below the surface. The He vertex will degenerate onto the plane of the ring in case we try to increase the number of the He atoms in the ring to six. This structure will produce a dimple with a curved surface of He atoms. The necessary geometry may be optimized using alkali–He and vertex–ring He distances as parameters. Figure 1 displays the structure schematically. We exclude the possibility of using more shells as we tacitly assume that van der Waals interaction is dominant in the nearest neighbour structure. Also we exclude taking non-integer number of shells as we do not consider surface vibrations and excluded the effect of zero point motions which is expected to give only minor corrections to the shifts. Error cancellation is likely to be not significant in this fixed cluster model.

Once the geometrical structure of the cluster is obtained the necessary quantum chemical calculations can be performed using different and sophisticated available techniques. The calculations have been performed both at the non-relativistic and relativistic

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