



Research paper

A CASPT2 study of the spectral shift of the resonance emission lines of Rb and Cs embedded in liquid He



Lucas Modesto-Costa^{a,b,*}, Prasanta Kumar Mukherjee^c, Sylvio Canuto^a

^a Instituto de Física, Universidade de São Paulo, Cid. Universitária, 05508-090 São Paulo, SP, Brazil

^b Departamento de Química, Instituto Militar De Engenharia, Praça General Tibúrcio, 80, 22290-270, Rio De Janeiro, Brazil

^c Department of Physics, Ramakrishna Mission Vivekananda University, P.O. Belur Math, Howrah 711202, West Bengal, India

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ABSTRACT

The emission line shifts of the resonance transitions ($s \leftarrow p$) of Rb and Cs embedded in liquid He environment have been estimated using CASPT2 with quadruple-zeta basis sets. The liquid He environment has been approximated by a spherically symmetric model cluster, with 14 He atoms placed in equidistant positions from the central alkali atom. The emission line for the D1 transition is found to be blue shifted. The shift is estimated to be -1.2 to -1.8 nm for Rb and -2.2 to -2.6 nm for Cs, in very good agreement with the experimental estimates of -1.2 nm and -2.1 nm respectively obtained in liquid He.

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1. Introduction

The spectroscopic characteristics of atoms and molecules in He [1,2] environment has been the subject of intense investigations for decades and the subject is rich both in terms of theoretical understanding and experimental findings [3,4]. Foreign particles embedded inside the liquid create a cavity or bubble-like structure due to strong Pauli repulsion, the shape and size of which are determined by the nature of the impurity and the angular momentum of the excited state [3]. The bubble size increases when the system is excited [5,6] and the relaxed bubble size is usually much larger compared to its initial dimension and it is also a function of external pressure, if any [7–11].

Recently experimental investigations have been performed on the absorption and emission spectra of alkaline-earth and alkali atoms in liquid helium by laser spectroscopic techniques [12–14]. Compared to the free atom the lowest $s \rightarrow p$ transition in alkaline-earth atoms, like Mg [12], Ca, Sr and Ba [13] embedded in helium shows spectral shifts of -3.7 nm, -2.7 nm, -3.3 nm and -4.3 nm, respectively. The shifts of the same transition for Rb and Cs, are -19 nm and -22 nm [14], respectively. Theoretical interpretation of the spectral line shifts and line profiles in absorption was initiated fairly successfully using the Standard Bubble Model

(SBM) [3]. Subsequently, relativistic cluster model calculations and methods based on sequential use of Monte Carlo simulation followed by quantum mechanics calculations (S-QM/MM) [15–18] have been very successful in interpreting the change in line positions and profiles connected with the absorption spectra of alkali and alkaline-earth atoms in liquid He. Recently, the excitation spectra involving $s \rightarrow s$ transition of Li and Na attached to the surface of He nanodroplets have been well described with non-relativistic CIS(D) and relativistic density functional methodologies using an asymmetric model cluster [19]. Barranco et al. [20] estimated the emission line shifts and line profiles of several alkali atoms in He nanodroplets using density functional theory along with Random Phase Approximation.

Although the available theoretical calculations have been successful in describing the spectral shift in the absorption for various atoms under liquid He, calculations for the interpretation of emission spectra of atoms under such confinement are rather scanty and are limited to a few alkaline-earth atoms using the SBM [12,21]. The basic difficulty for the theoretical estimation of the emission spectra lies in the fact that after absorption, the bubble size increases resulting in a shift of the energy minimum of the excited state potential with a substantially higher radius of the cluster [3]. The emission wavelength is usually red shifted with respect to the free transition, as was found for Mg, Ca and Sr [12,13]. Due to non-availability of accurate excited state pair potential in liquid He environment, precise calculation of the emission spectral wavelength becomes more difficult. Moreover, such

* Corresponding author at: Instituto de Física, Universidade de São Paulo, Cid. Universitária, 05508-090, São Paulo, SP, Brazil.

E-mail address: lucmod@if.usp.br (L. Modesto-Costa).

shifts are usually much smaller compared to those of the absorption spectra as it was observed for Ca, Sr and Ba to be less than 1 nm [13]. Mg has a shift of 3.2 ± 0.2 nm for the emission line ($3s^2: 1S \leftarrow 3s3p: 1P$) with FWHM of 3.3 nm [12]. A calculation using the standard bubble model (SBM) with adiabatic line-broadening theory shows a shift in the emission of the same atom of only 1.1 nm [21]. For Rb and Cs, the resonance emission line is blue shifted in liquid He [14]. For Rb, the experimental D1 line shows a shift of -1.2 ± 0.2 nm with HWHM of 0.9 ± 0.2 nm while that for Cs it is -2.1 ± 0.2 nm with HWHM of 1.2 ± 0.2 nm [14]. Signals of the D2 emission line of Rb in liquid He have not been detected, while that of Cs shows a very large width with a typical splitting [14]. Indeed, for Cs, the emission spectrum in the D2 region is composed of two bands, in which one resembles the free atomic transition with shift of 0 ± 1 nm having HWHM of 1 ± 1 nm. The second band is shifted by 6 ± 2 nm with a large width (HWHM of 12 ± 2 nm). Similar effect was observed also in the absorption profile. This splitting of the D2 band is interpreted as due to dynamic Jahn–Teller effect resulting from the non-spherical distribution of the liquid He surrounding with consequent symmetry lowering of the electronic states [6,14,22].

In the current work we present the results of our investigation for the emission spectra of Rb and Cs, embedded in liquid He(II) using a cluster model. For the absorption spectra, the cluster model estimates of the shifts compare well with those obtained using the S-QM/MM [15–18] methodology. Due to dominating van der Waals interaction between He and the central atom only nearest neighbors are mostly effective in producing the shift. Hence, the basic advantage here is the relatively small number of He atoms surrounding the central foreign atom to represent the cluster and its symmetry ensuring efficient calculation [16,23,24]. This model ignores the structural fluctuation of the liquid He atoms around the mean position and hence the width of the spectral lines cannot be calculated [16]. Calculation for the line shifts in the emission spectra is more challenging due to the larger cluster radius resulting in a substantial increase in the number of He atoms surrounding the central foreign atom. Further the angular momentum of the excitation is likely to render non-spherical distribution of nearest neighbors [25]. We have taken an approximate spherically symmetric cluster to attempt estimation of the spectral line shifts of Rb and Cs in emission. Excited states of the gas phase and the cluster have been calculated by using the Complete Active Space Perturbation Theory (CASPT2) [26] with large quadruple zeta basis sets. This method has proven its efficacy to describe molecular excited states with good accuracy and relatively low computation cost [26,27]. Spin–orbit coupling has been incorporated in this study to estimate the shift of the D1 and D2 lines of alkali atoms in the emission. One major difficulty is to assign correctly the size of the active space [28], balancing the emission in the gas phase and in the model cluster due to surrounding He atoms. The pair potential, existing in the literature for Rb–He and Cs–He in their ground and excited states [29–33], have been utilized here. We choose the radius of the cluster based on the minimum of the excited state potential curve ($A^2\Pi_{1/2}$) of alkali–He pair, which has a larger value compared to that of the ground state ($X^2\Sigma_{1/2}^+$). The calculated emission line position of free Rb is found to be in excellent agreement with the experimental data but for Cs the results differ by ~ 20 nm. The shift of the D1 line in the emission in the embedded system will be found in good agreement with the experimental data, for both Rb and Cs.

2. Methodology

The effect of the liquid He environment on the embedded alkali atoms (Rb and Cs) has been modeled by using a symmetric cluster with 14 He atoms arranged in two shells, Fig. 1. The first shell is

formed by eight He atoms placed at the corners of a cube of edge length a that is taken to be equal to the He–He distance in the dimer. The second shell contains six He atoms placed at the center of the six faces of another larger cube of edge length $a\sqrt{3}$, both having the center at the position of the alkali atom. In this structure, the distance between the alkali atom and each He atom is the same R_{X-He} . This symmetric configuration of He atoms acts as a perturbation through the pair potential existing between He and the alkali atom and is an approximation to the effect of bulk liquid surrounding. The efficacy of this model has been well tested in calculating the shift of the absorption lines for various alkali and alkaline earth atoms in liquid He which compares well with experimental data and also with those obtained from the more realistic S-QM/MM [15–18] calculations. In this calculation we assume that there is time enough for the structural relaxation of the excited state to occur [14,34,35] and hence in the emission calculation we have optimized the cluster size using the excited state of alkali–He pair potential. To have an accurate representation of the excited states, quantum mechanical calculations have been performed in the following way: a Complete Active Space Self-Consistent Field (CASSCF) calculation has been performed first to obtain the starting wave function for a subsequent CASPT2 [26] calculation using the Molcas 7.8 package [36] to yield the final result. The active space has been obtained by selecting orbitals of s and p symmetry. The minimal space includes one partially occupied $5s$ and full occupied $4p$ orbitals for Rb and $6s$ and $5p$ orbitals for Cs, the next unoccupied orbital is $5p$ for Rb and $6p$ for Cs. To supplement the active space occupied and unoccupied orbitals have been included subsequently to improve the results of the wavelength in emission. Different active spaces were used and the results analyzed. All the electronic wave functions of alkali and He atoms have been represented in terms of the atomic natural orbital (ANO) type basis set named ANO–RCC–VQZP, where all electrons have been included and the primitive and contracted forms are ($26s22p15d4f2g/9s8p4d3f2g$) for Cs, ($23s19p11d4f2g/8s7p4d2f1g$) for Rb [37] and ($9s4p3d2f/4s3p2d1f$) for He [38]. To account for the spin–orbit coupling relativistic correction was obtained based on the Douglas–Kroll Hamiltonian [39,40].

3. Results

First, we present the results for the free atom emission spectra of Rb and Cs. Using different combination of active space in the CASPT2 calculations we obtain the wavelength of the characteristic

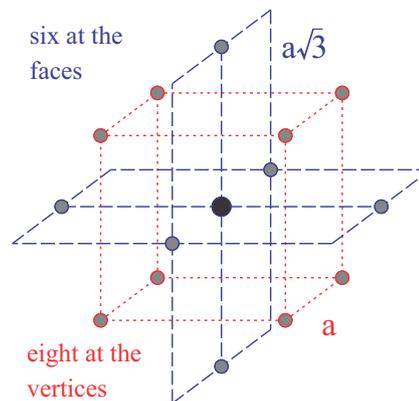


Fig. 1. Symmetric cluster with the centered alkali and He atoms surrounding in two shells. The first shell is formed by the eight He atoms at the vertices of a cube with edge equal to a (red dashed cube). The second shell is formed by six He atoms at face centered of cube of edge equal to $a\sqrt{3}$ (blue dashed cube). The final structure has each pair He–alkali at the same distance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

emission line of Rb and Cs, displayed in Tables 1 and 2 respectively. The results compare well with the experimental findings. The experimental D1 and D2 lines of Rb are respectively at 794.76 nm and 780.03 nm [14] with a separation of 14.73 nm. As mentioned, in our calculation the spin-orbit coupling was included, allowing the estimation of the D1 and D2 line separation. The best estimate of the free line of Rb is obtained by using an active space with 15 electrons in 11 orbitals ($3p4s4p5s-5p$), which is near to our computational limit. We obtain the emission D1 line at 795.78 nm and D2 at 786.99 nm, in very good agreement with experiment but a slight underestimate of the separation. All the results with different active spaces indicate good values for the calculated emission, especially in the cases where a large number of occupied orbitals have been used. Inclusion of the spin-orbit coupling is still insufficient to improve the difference between the D1 and D2 lines calculated between 9 and 11 nm in comparison to the experimental difference of 14.73 nm.

For Cs, the agreement with the experimental result for the emission line position is not as good as for Rb. The wavelength of the D1 line of Cs has been estimated within the range 913–943 nm depending on the active space and overestimating the experimental result of 894.35 nm [14]. Similarly, the D2 line position ranges from 888 nm to 913 nm, while the experimental value is 852.11 nm [14]. This may be attributed to the more complex nature of the Cs atom with its inner shell structure in which relativistic corrections are more prominent indicating appreciable changes compared to Rb–He system. Inclusion of spin-orbit interaction is insufficient to account for the difference of 42.24 nm. However, consistent behavior is noted by changing the number of active electrons. From the minimal active space, the emission wavelength decreases as a function of the number of electrons included for Cs and Rb. The increase of virtual orbitals shows inconsistent oscillatory behavior in the emission wavelength, as displayed in Tables 1 and 2.

The next step now is to obtain the size of the He bubble forming the cluster that mimics the He interaction. The radius of the cluster increases in the excited states and the electronic levels of atomic probes are dependent of this size. As a first alternative, one can utilize the CASPT2 calculation to obtain the potential for the first excited state. However the calculations showed a discrepancy in the potential curves for distances greater than 8 Å. Consequently, as an alternative, we used the potential energy curve of Blank et al. [29], to obtain the size of the cluster. The alkali–He pair potential of the ground and first excited states have been calculated using spin-orbit coupled multi-reference singles and doubles

Table 1
CASPT2 calculations of the emission spectra of free Rb and the shift under liquid He using a cluster model. All results in nm. Different active spaces are used, as shown.

Active space	Free atom		Shift		
	D1	D2	D1	D2	D2'
4p5s-5p (7,7)	798.92	790.15	-1.44	-1.51	-1.52
4p5s-5p6s (7,8)	797.59	788.69	-1.43	-1.50	-1.51
4p5s-5p6s6p (7,11)	800.80	789.71	-1.45	-1.54	-1.60
4p5s-5p6s6p7s (7,12)	815.19	805.75	-1.64	-1.72	-1.72
4p5s-5p6s6p7s7p (7,15)	806.74	795.84	-1.58	-1.65	-1.67
4s4p5s-5p (9,8)	796.50	787.70	-1.45	-1.53	-1.54
4s4p5s-5p6s (9,9)	799.14	789.49	-1.47	-1.54	-1.56
4s4p5s-5p6s6p (9,12)	803.97	792.52	-1.47	-1.55	-1.57
4s4p5s-5p6s6p7s (9,13)	814.99	804.36	-1.81	-1.89	-1.89
3p4s4p5s-5p (15,11)	795.78	786.99	-1.24	-1.32	-1.33
3s3p4s4p5s-5p (17,12)	796.05	787.25	-1.29	-1.37	-1.38
Experimental [14]	794.76	780.03	-1.2 ± 0.2	n/a	n/a

Active space definition: (a, b) a is the number of electrons and b is the number of orbitals. For Rb, the 5s orbital has 1 electron and the inner orbitals are fully occupied.

Table 2

CASPT2 calculations of the emission spectra of free Cs and the shift under liquid He using a cluster model. All results in nm. Different active spaces are used.

Active space	Free atom		Shift		
	D1	D2	D1	D2	D2'
5p6s-6p (7,7)	922.31	896.94	-2.30	-2.63	-2.65
5p6s-6p7s (7,8)	913.49	888.48	-2.31	-2.63	-3.18
5p6s-6p7s7p (7,11)	924.46	892.64	-2.20	-2.57	-2.57
5p6s-6p7s7p8s (7,12)	941.26	913.27	-2.63	-2.92	-2.94
5s5p6s-6p (9,8)	921.98	896.36	-2.24	-2.57	-2.58
5s5p6s-6p7s (9,9)	925.21	897.22	-2.28	-2.62	-2.62
5s5p6s-6p7s7p (9,12)	931.99	899.06	-2.35	-2.71	-2.75
5s5p6s-6p7s7p8s (9,13)	943.33	911.78	-2.65	-2.94	-2.99
4p5s5p6s-6p (15,11)	921.13	895.53	-2.44	-2.76	-2.80
4p5s5p6s-6p7s (15,12)	920.74	893.82	-2.35	-2.62	-3.85
4s4p5s5p6s-6p (17,12)	921.45	895.83	-2.34	-2.66	-2.68
Experimental [14]	894.35	852.11	-2.1 ± 0.2	0 ± 1	6 ± 2

Active space definition: (a, b) a is the number of electrons and b is the number of orbitals. For Cs, the 6s orbital has 1 electron and the inner orbitals are fully occupied.

configuration interaction (SOC) [39,40]. Relativistic pseudo-potential basis set for alkali and triple zeta basis set for He has been adopted. The ground state ($X^2\Sigma_{1/2}^+$) potential of Rb–He shows a minimum at 6.61 Å. This is consistent with our previous studies of the same cluster using time-dependent density functional theory (TDDFT) with different functionals (O3LYP and PBE1PBE) and basis sets (DZP and def2-QZVP) resulting in a cluster radius between 6.2 Å and 6.8 Å [18]. For the Cs–He cluster the minimum is found to be located at 6.93 Å and TDDFT calculations indicate a size of 6.5–6.7 Å [18], while relativistic density functional calculation shows a minimum at 5.7 Å [41]. Classical Monte-Carlo simulations indicate [18] that the first solvation shell of Rb in liquid He is composed of 53–57 He atoms, with the maximum at 6.7–7.0 Å. For Cs, the first shell is formed by as much as 58 He atoms and has a maximum at 7.0 Å [18].

The potential energy curve in the excited states is discussed now. The $A^2\Pi_{1/2}$ potential corresponding to the D1 transition shows two minima at different places. One appears at a smaller distance compared to that of the ground state minimum, corresponding to 3.12 Å for Rb–He and 3.44 Å for Cs–He [29]. A cluster with this radius appears to be inappropriate. The distance of the second minimum is larger than that of the ground state and is at 9.10 Å for Rb–He pair and 9.21 Å for Cs–He pair. The potential barrier at this point is very small, only 21 cm⁻¹ for Rb–He and 60 cm⁻¹ for Cs–He indicating the inherent difficulty in finding the minima [29]. We believe that after absorption, the size of the cluster increases from somewhat below 7 Å to above 9 Å, the minimum obtained for the excited state alkali–He pair. The other excited state of the pair $A^2\Pi_{3/2}$, is a smooth curve without showing a noticeable minimum beyond that of the ground state.

We investigate now the shift of the emission line in the cluster environment. In Table 1 we display the shift of the D1 and D2 emission lines for Rb surrounded by He atoms. Experimentally, a shift of -1.2 ± 0.2 nm is observed for the D1 line of Rb in liquid He, while the D2 line has too small an intensity to be detected [14]. The values are consistent with that of the isolated alkali atom, and the shifts are similar with different choices of the active space. Numerically the spectral shift of the D1 line varies from -1.2 nm to -1.8 nm. The inclusion of more electrons in the active space has no effect in the estimated shift. For the D2 line, the behavior of the shift is similar. Generally, there is an increase of at most 0.1 nm in shift values, compared to the shift in D1 line. A very small splitting in the D2 line due to symmetry breaking is observed, labeled as D2' in Tables 1 and 2. The difference between D2 and D2' is negligible in most case, with a maximum of 0.1 meV for Rb and 1.9 meV for Cs. In the cluster model the calculation of the

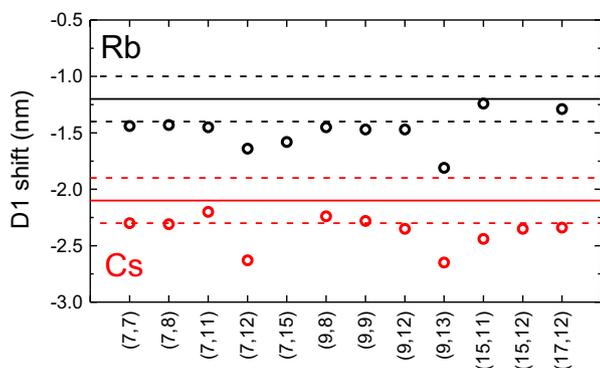


Fig. 2. Emission shift of D1 line of Rb (black data) and Cs (red data) in cluster model of 14 He atoms using CASPT2 and ANO-RCC-VQZP basis set. The horizontal continuous is the experimental shift, while the dashed line is the uncertainty of the experimental value for each alkali atom. Each circle is the emission calculated with a specific active space defined by active space size (electrons, orbitals). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

width of the emission band is not possible directly because the structural fluctuations of the He atoms are ignored. Hence we report only the shifts in the emission. However, the width can be estimated using the fluctuations of the He atoms from their equilibrium positions due to finite temperature [24].

The D1 emission line shifts in Cs cluster are displayed in Table 2 and are found to vary from -2.2 nm to -2.6 nm. The shift shows a similar trend, for both Rb and Cs, as can be seen in Fig. 2. The line shift is consistent when more electrons are include in active space, but inclusion of more unoccupied orbitals shows small variation. Even with this small fluctuation in shift values, the shift appears to be in excellent agreement with the experimental data (-2.1 ± 0.2 nm), albeit a difference exists for the emission line position in gas phase. Actually, we believe that the difference in the calculation for free alkali is reflected in a similar manner in the cluster calculation. For this reason the calculation for the shift is more accurate because the errors in gas phase and cluster calculation would likely to be canceled in a shift estimation. Interestingly in this case the shift in the D2 line is observed experimentally with a marked splitting [12]. The new line D2' has a very large width, 12 ± 2 nm, and the difference between the splitting of the lines (D2 and D2') is ca. 6 nm. No splitting is observed in our calculation which incorporates the spin-orbit coupling. Again, incorporation of proper symmetry in our cluster model may give an insight of the shift of D2 and D2' in He environment.

As expected, increasing the radius of the cluster decreases the calculated shifts. In the case of Cs, for instance, increasing the radius from its calculated equilibrium value of 9.2 \AA to 9.3 \AA decreases the shift by ca. 0.3 nm, i.e.; from -2.3 nm to -2.0 nm. An equivalent increase in the cluster radius surrounding the Rb varies the shift from -1.5 nm to -1.3 nm. In both cases, the small active space has been used.

4. Conclusions

Theoretical interpretation of the emission spectra of alkali atoms Rb and Cs embedded in liquid He has been obtained using a simple but efficient cluster model comprising 14 He atoms arranged in a symmetric manner with respect to the central alkali atom. The size of the cluster in the excitation was based on Blank et al. [27] that calculated the potential energy curves for alkali-He system using spin-orbit coupled multi-reference singles and doubles configuration interaction. The CASPT2 method has been found

to be very effective in obtaining such interpretations corroborating very well with the experimental observations, particularly for the D1 line. The D2 line suffers a splitting due to dynamic Jahn-Teller effect arising out of the interaction of the excited complex. The symmetry of the current cluster does not allow splitting of the D2 line, as observed experimentally in the case of Cs. The emission line for the D1 transition is found to be blue shifted. The results are independent of active spaces, since the ratio of orbitals and electrons is not over balanced. The shift is estimated to be -1.2 to -1.8 nm for Rb and -2.2 to -2.6 nm for Cs, in very good agreement with the experimental estimates of -1.2 nm and -2.1 nm respectively under liquid He confinement.

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