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Theoretical study of the spectral shift of the absorption line of Rb and Cs in liquid helium

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ABSTRACT

A combined and sequential use of Monte Carlo simulation and time-dependent density functional theory is made to obtain the excitation line shifts and widths of Rb and Cs embedded in liquid ^{4}He. In each case calculations are made on 100 statistically uncorrelated configurations with Rb (Cs) surrounded by nearly 60 He atoms treated explicitly. Different basis sets and functionals are used for obtaining the blue shifts of the absorption lines $5s \rightarrow 5p$ of Rb and $6s \rightarrow 6p$ of Cs. Estimate of the line broadening is also made and results for both the shift and broadening are obtained in good agreement with experiment.

1. Introduction

Liquid helium has been of interest since many years because of its unique physical properties. Extensive investigations have been performed on liquid helium for several decades due to the extraordinary properties associated with the superfluid phase below the critical temperature of 2.17 K [1] for ^{4}He. Considerable interest has been generated in recent years for the study of the quantum fluid properties [2]. Currently, additional interest has been devoted for the study of the spectroscopic properties of foreign atoms embedded in liquid helium [3–9], which was much facilitated by the advances in implantation techniques [10]. Different techniques are possible and are discussed by Tabbert et al. [11]. The general observations from the experimental data are that the spectral line shifts compared to the free atomic systems, and there are also a broadening of the spectral lines, changes in the line profiles, reduction of ionization potentials of the central atom, quenching of certain spectral lines and the appearance of transitions forbidden in the free system [11].

Theoretical studies were first based on the Standard Bubble Model (SBM) of the liquid surrounding the foreign atom [12]. It is assumed that the central atom resides in a cavity, formed due to the strong Pauli type repulsion at the liquid boundary. The size and shape of the cavity depend on the angular momentum of the central atom and the atom–liquid pair potential, the typical diameter being 8–12 Å [10,13]. The SBM utilizes the classical expression for the liquid energy and the atom–liquid interaction is constructed from the atom–He pair potential suitably weighted over its density distribution [11]. Theoretical attempts to estimate the spectral properties of the atom based on the SBM are rather scanty [13,14] but with a fair success in some cases. Experimental data indicate relatively large shifts of the resonance lines of the higher members of the alkali atoms like Rb and Cs [6,11], but apparently not observed for the lower members Li, Na and K. The trend of the shift is physically expected due to the loosely bound character of the valence electrons of such systems. In recent years attempts have been made to interpret the excitation spectra and line profiles of alkali atoms like Na, Rb and Cs based on phenomenological density functional approach [15,16] as well as non-relativistic and relativistic *ab initio* quantum chemical methods [17–20]. A review on the different theoretical methods adopted for interpreting the experimental data is due to Coutinho et al. [21]. The first *ab initio* calculation was apparently made by Ludwig et al. [17] utilizing the Monte Carlo (MC) simulation technique to generate the liquid helium structures around the central Na atom. Subsequent quantum mechanical (QM) calculations [17] using these structures have been performed for obtaining the spectral line shift of the D line of Na using the time-dependent density functional theory (TD-DFT) with different exchange correlation functional. Successful investigation on the spectral line shift and line profile for the alkaline earth atoms, Be, Mg, Ca, Sr and Ba have also been performed by Modesto-Costa et al. [22] using the same methodology. Further, a calculation of the spectral line shift of Na dimer in liquid helium [23] obtained very good agreement with existing experimental data [6] both in the shift and in the line width of the principal band. Attempts have also been made for estimating such line shifts in alkali atoms using

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a fixed cluster model. Symmetry Adapted Cluster–Configuration Interaction (SAC–CI) has been successfully applied by Saha et al. [18] for the estimation of the excitation line shift of the D line of Na. For Na, Rb and Cs relativistic density functional theory [19,20] with a fixed cluster representation of the helium atoms surrounding the central alkali atom has been applied. This latter method has been successful in predicting the experimental line shifts [24] in Rb and Cs under such conditions. The MC simulation technique followed by QM calculations appears to be more realistic than the fixed cluster model because it considers the statistical nature of the liquid at finite, though low, temperature and also for providing information about line profiles.

The success of the sequential use of Monte Carlo simulation followed by TD-DFT calculations suggests extending the investigation of the spectral properties of the liquid helium embedded alkali atoms to the heavier and more challenging Rb and Cs. For these two atoms accurate experimental values are available [6] but theoretical studies not only are scarce but also limited to the spectral shifts [20] without explicit consideration of the line broadening. The absorption spectra of Rb and Cs have been studied by Takahashi et al. [6] in the helium superfluid region. Our theoretical model cannot consider the superfluid nature. However, according to previous experimental results [7] no spectral changes are observed in the optical spectra when the liquid goes from normal to superfluid liquid. That is, the spectral changes are insensitive when crossing the critical point of liquid helium. We assume that this is also approximately correct for the band width. Our work incorporates the effects of the helium environment at a temperature only slightly above the lambda point. In gas phase, the spectral lines of the absorption $5s \rightarrow 5p$ of Rb and $6s \rightarrow 6p$ of Cs are well defined. Due to the spin–orbit coupling, Rb shows the D1 line at 794.8 nm and D2 line at 780.0 nm, while for Cs, the D1 line is at 894.4 nm and the D2 is at 852.1 nm [6]. When embedded in liquid helium the spectral lines shift to lower wavelengths. The line width increases appreciably due to the interaction with the surrounding liquid He. For the D1 line, a shift of −16.8 nm is observed for Rb, while for Cs it is −18.4 nm [6]. The line profile for the D2 absorption is peculiar with a splitting into two lines with asymmetric shapes and relatively less intensity compared to the corresponding D1 line profile. Hence, the line profile of the D2 transition has two peaks showing the shifts of −16.0 nm and −24.0 nm for Rb and −18.1 nm and −30.1 nm for Cs [6].

In this work we will report a detailed theoretical investigation of the spectral shifts of the principal $s \rightarrow p$ lines of the heavy alkali Rb and Cs atoms in liquid helium environment. As in previous work we combine MC simulation and TD-DFT using different existing pair potentials, sophisticated basis sets and exchange correlation functional. The MC simulation is used to generate the configurations (atomic positions) of the helium atoms around the alkali in the corresponding thermodynamic condition. Next, configurations are sampled for the subsequent QM calculations of the spectra. The sampling is obtained by using the statistical correlation to ensure fast statistical convergence. In addition, for comparison, we will later use a cluster model obtained by geometry optimization of the alkali atom surrounded by a small number of He atoms.

2. Methodology

The configurations of liquid helium surrounding the central alkali atom X (X = Rb and Cs) are generated using MC simulation with Metropolis sampling technique [25] in the NPT ensemble. The temperature is kept fixed at 3 K, slightly above the lambda point. The pressure used is 1 at. The MC simulation technique utilizes the Lennard–Jones pair potentials and the liquid structures generated depend on the pair potentials. To this end we have chosen two sets of standard pair potentials of alkali–He, the first is due to Patil [26] and the other is due to Kleinekathöfer et al. [27], this latter being referred to as KTTY potential. The He–He pair potential was that consistently used in our earlier calculations [17,22,23], and has been obtained from CCSD(T) calculations with high quality correlations consistent cc-pV5Z basis set [28]. In all cases 999 He atoms are allowed to interact with one alkali atom.

Among the large number of configurations generated in the MC simulation, the configurations adopted for subsequent QM calculations are statistically uncorrelated and are obtained after calculating the auto-correlation function of the energy [29]. This is a hybrid procedure termed as sequential Monte Carlo/quantum mechanics (S-MC/QM) methodology [30]. The success of this methodology was amply demonstrated in predicting solvent effects of organic molecules in different solvents [30,31]. The MC simulation and the interface for subsequent QM calculation were made using the Dice program [32]. The TD-DFT calculations have been performed with the Gaussian 03 program [33]. Several exchange correlation functional were adopted but better results have been obtained with O3LYP [34] and PBE1PBE [35]. The details of the basis sets used and results obtained are discussed in the next section.

Using the local density approximation relativistic density functional theory (RLDA), have been previously applied [19,20]. Using a fixed cluster model of helium atoms surrounding the central alkali atom the shift of the excitation lines in Rb and Cs were obtained [36]. Analysis of the applicability of this non-relativistic cluster model will also be made.

3. Results and discussion

The main goal of the current report is thus to describe the spectral line shifts and line widths of the principal resonance transitions for higher members of the alkali atoms, Rb and Cs, in liquid helium. Toward this end we use the S-MC/QM methodology using currently available pair potential and sophisticated basis sets. For such systems accurate laser spectroscopic data exist [6]. For the QM calculation of the shift and width we considered the 6-311++G(2d,2p) as well as the cc-pV5Z basis sets for He while for Rb we have used DZP [37] as well as def2-QZVP basis set due to Weigend and Ahlrichs [38]. For Cs only results with this basis set [38] will be shown. The DZP basis set used is an efficient all-electron contracted Gaussian basis set of double-zeta valence quality plus polarization functions developed by Jorge and co-workers [37]. Several test calculations showed that the use of the cc-pV5Z basis for He considerably increases the computational time without any significant change of the results. So we will only present the results obtained using the 6-311++G(2d,2p) basis for He.

The radial distribution functions obtained from the MC simulation of the alkali atom in liquid helium are shown in Figure 1. Three MC simulations are performed, one for Cs in helium and two for Rb in helium, corresponding to the two different potentials used for the Rb–He interaction. In every case, Figure 1 shows three solvation shells. Using the KTTY [27] or Patil [26] potentials give small distinctions in the distribution of helium around the central Rb atom. Because of the finite range of the interatomic potentials in the subsequent QM calculations we will consider only the first solvation shell. For the KTTY Rb–He potential, the first solvation shell starts at around 5.9 Å, ends at 8.2 Å and has the maximum at 7.0 Å, comprising a total of 57 He atoms surrounding the central Rb. In sampling configurations for the subsequent TD-DFT calculations to obtain the $5s \rightarrow 5p$ transition we will use explicitly this first solvation shell comprising 57 He atoms surrounding the Rb atom. Similar selection and QM calculations are made for the other cases (using the Patil interatomic potential for Rb–He and Cs–He). In all calculations we have used 100 such configurations for evaluating the average shift

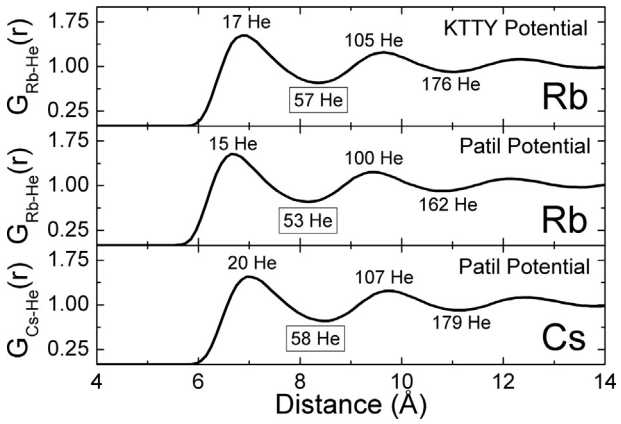

Figure 1. Radial distribution function of liquid simulation of the alkali atom embedded in liquid He using the KTTY [27] potential for Rb and the Patil [26] potential for Rb and Cs. The number of He atoms at the maximum and at the end of each shell is indicated.

and also the width. As mentioned before the configurations have been selected using the auto-correlation function of the energy [29] to ensure that converged values of the electronic transition energies are obtained. The half width at half maximum (HWHM) can be obtained from the standard deviation σ using $\sigma\sqrt{2\ln 2}$. The results obtained using different basis sets and correlation functionals are shown in Table 1. Each theoretical value shown in Table 1 is the result of a statistical analysis after 100 QM calculations of a system composed of one alkali atom surrounded by the entire first solvation shell (for instance, Rb surrounded by 57 He atoms in the case of the KTTY potential). Thus considering all theoretical values shown in Table 1, a total of 1000 QM calculations have been performed. This large number precludes the use of relativistic calculations but allows a good description of the inhomogeneous broadening necessary to treat the line width. Theoretical values are then compared with the experimental results [6]. Our non-relativistic calculations only yield the mean D line. However, the experiments show the line shifts and profiles of the separate D1 and D2 lines. In liquid helium, the excitations resulting in the D2 transition form a broad asymmetric band with less intensity than that corresponding to the D1 band. In fact, the experimental results [6] even indicate a splitting of the D2 line. The origin of the splitting is discussed in terms of the symmetry reduction [6] by the non-spherical density distribution of surrounding helium atoms. Thus the comparison between our theory and the experiment needs additional considerations. As our calculations cannot distinguish the D1 and D2 lines the experimental results are reported in Table 1 as an interval, corresponding to the unresolved D line. However, as the D1 line is more intense in this case, the unresolved result is expected to be closer to the lower limit of the interval shown in Table 1. For instance, the spectral shift of the D1 line in the case of Rb is −16.8 nm. From a close look, we find that the result of −15.2 nm using KTTY potential and the DZP basis with O3LYP functional agrees well but it slightly underestimates the experimental data. The result of −16.0 nm using the PBE1PBE functional with the def2-QZVP basis appears also to be consistent but the result of −20.1 nm obtained with the DZP basis and PBE1PBE functional is well within the experimental range, considering that we cannot distinguish the D1 and D2 lines. Using the Patil potential [26] for the Rb–He interaction in the MC simulation, the first solvation shell starts at 5.8 Å, ends at 8.1 Å with a maximum around 6.7 Å encompassing 53 He atoms. In this case of Rb very good results are obtained using the Patil potential with the def2-QZVP basis set and the O3LYP functional. The collection of results presented in Table 1 indicates some differences in the calculated spectral shifts but consistent and good results are obtained in all cases, with the sole exception of the very small value of −8.2 nm obtained with the O3LYP functional, KTTY potential and def2-QZVP basis set.

For the Cs–He system the liquid simulation was made using the Patil potential only. In this case the QM calculations used the effective core potential (ECP). The radial distribution function plotted in Figure 1 indicates the beginning of the first solvation shell at 6.0 Å ending at 8.5 Å with the peak at 6.95 Å encompassing 58 He atoms. Quantum mechanical calculations have been performed with def2-QZVP basis with the two functionals O3LYP and PBE1PBE. The spectral line shifts have been evaluated from the distribution of the results obtained using the 100 configurations selected from the MC simulation. The width has been obtained in a similar manner as it was done for Rb–He system. The values shown in Table 1 compare favorably with existing experimental and other theoretical results [19,20,35]. For the Cs–He system we find good agreement with both the O3LYP and PBE1PBE functionals but a slight better agreement of the shift of the D1 line can be seen for the O3LYP/def2-QZVP model. All-electron calculations for Cs atom is computationally very demanding due to the large number of electrons but the results using ECP appear to be consistent.

We now discuss the results for the spectral widths. In an atomic case, there is no vibrational contribution to the broadening and in fact it comes mostly from the inhomogeneous distribution. From the ensemble of calculated transition energies and intensity values it is possible to obtain the width at half maximum. The calculated values are also shown in Table 1. The results indicate that all theoretical values obtained for both Rb and Cs are in relatively good agreement with experiment but a systematic overestimation can be seen.

Table 1
Comparison of theoretical and experimental results of the resonance transition $s \rightarrow p$ of Rb and Cs.

System	Potential	Functional	Alkali basis set	Free	Shift	HWHM
Rb–He $5s \rightarrow 5p$	KTTY	O3LYP	DZP	899.4	−15.2	10.0
			def2-QZVP	908.8	−8.2	9.2
		PBE1PBE	DZP	874.4	−20.1	8.5
			def2-QZVP	869.3	−16.0	8.1
	Patil	O3LYP	DZP	899.4	−23.4	11.5
			def2-QZVP	908.8	−16.4	10.9
		PBE1PBE	DZP	874.4	−27.2	9.5
			def2-QZVP	869.3	−23.2	9.3
		Experiment		787.3[a]	[−16.8, −24.0][b]	5.0[c]
Cs–He $6s \rightarrow 6p$	Patil	O3LYP	def2-QZVP	1035.7	−17.4	14.6
		PBE1PBE	def2-QZVP	980.0	−25.8	12.7
		Experiment		866.2[a]	[−18.1, −30.1][b]	5.4[c]

The basis set adopted in He is 6-311++G(2d,2p) and the HWHM was based on the standard deviation (see text). Values are in nm.

[a] Average of the D1 and D2 lines of the free atom [6].

[b] Range involving the separate shifts of the D1 and D2 lines [6].

[c] Average of the D1 and D2 lines. For reference, the values of the half width for the D1 lines are 4.0 ± 0.5 nm (Rb) and 5.5 ± 0.5 nm (Cs).

Table 2
Optimized cluster of 14 helium atoms in a symmetric alignment around the He atom, using different functionals and basis sets to estimate the spectral shift of $5s \rightarrow 5p$ of Rb and $6s \rightarrow 6p$ of Cs.

System	Functional	Alkali basis set	R_{min} (Å)	Shift (nm)
Rb–He $5s \rightarrow 5p$	O3LYP	DZP	6.45	−15.3
		def2-QZVP	6.19	−22.4
	PBE1PBE	DZP	6.67	−11.0
		def2-QZVP	6.40	−20.0
	Experiment			[−16.8, −24.0][a]
Cs–He $6s \rightarrow 6p$	O3LYP	def2-QZVP	6.53	−23.6
	PBE1PBE	def2-QZVP	6.69	−21.3
	Experiment			[−18.1, −30.1][a]

The He basis set is 6-311++G(2d,2p).
[a] Range involving the separate shifts of the D1 and D2 lines [6].

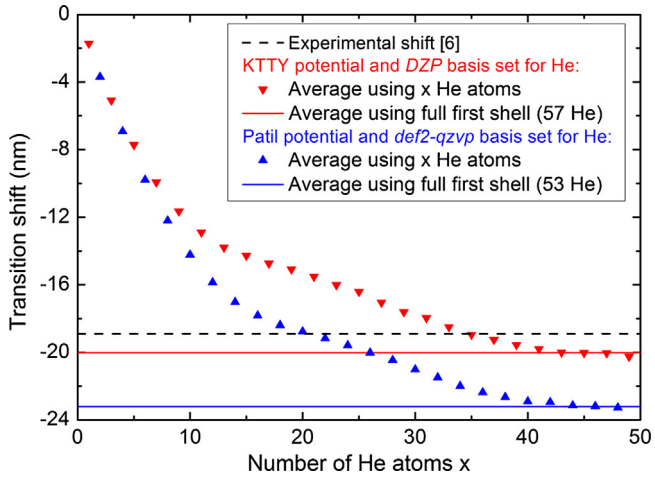

Figure 2. Convergence of the calculated transition energy shifts of Rb with the number of helium atoms explicitly included in the QM calculation. Every entry is the result of an average excitation energy obtained with 100 quantum-mechanical calculations using the PBE1PBE functional.

All results obtained for the transition energies are statistically converged. Another issue is the convergence of the results with respect to the number of helium atoms used in each configuration. Figure 2 shows the convergence of the spectral shift of Rb as a function of the number of nearest neighbor helium atoms and the PBE1PBE functional. The convergence with size is obtained before we reach the number of fifty helium atoms surrounding the alkali atom, thus before the number of explicit helium atoms used in every case, assuring convergence also with respect to the number of environmental atoms used.

Now, for comparison, we analyze the small cluster model to evaluate the spectral line shift where just one QM calculation is used. The cluster consists of a fixed structure composed of some helium atoms surrounding the central alkali atom. This will indicate the usefulness of non-relativistic cluster model and compare with the sequential MC/QM model so as to be a viable alternative. Similar to a previous study [20] we have used the spherically symmetric distribution of 14 He atoms, eight at each corner of a cube and six on the top of the faces such as to maintain the same distance from the central alkali atom. Calculations have been performed with the optimized geometry of the clusters using similar exchange correlation functional and basis sets. The results are displayed in Table 2. The optimized Rb–He and Cs–He distances can be compared to the maximum of the radial distribution function obtained in the liquid simulation. It can be noted that in all cases the Rb–He and Cs–He distances are shorter than the value obtained for the maximum of the distribution obtained in the liquid case, that is close to 7.0 Å in both cases, as seen in Figure 1. The decreased distance is, of course, a consequence of the energy minimization that maximizes the interatomic interaction. The distances obtained with the DZP basis are closer to the X–He obtained in the MC simulation and larger than that obtained with the def2-QZVP basis. But the results for the line shift in Rb–He and Cs–He clusters compare favorably with the experimental values and also with existing RLDA results for the spectral shifts of −15.4 nm and −16.7 nm [20].

4. Conclusions

A combined use of Monte Carlo simulation and non-relativistic quantum mechanical calculations to obtain the spectral line shift of Rb and Cs in liquid helium environment has been presented. The transition energies are obtained using time-dependent density functional theory. Different functional and basis sets are used and a consistent picture of the blue shifts of the absorption lines $5s \rightarrow 5p$ of Rb and $6s \rightarrow 6p$ of Cs are obtained. With an explicit thermodynamic condition used in the Monte Carlo simulations, 100 statistically uncorrelated configurations are sampled which allows also to estimate the line broadening. For the He–alkali interaction two potentials were used and the distributions of helium atoms around the central alkali are only slightly different, including 50–60 helium atoms in the first solvation shell. The convergence of the spectroscopic results is verified both with respect to the number of configurations used as well as the number of helium atoms used to represent the environment around the alkali atom. Good results are obtained as compared to the experimental values both for the line shifts and widths, but this latter is systematically overestimated. Similar calculations indicate that the spectral lines obtained with the Patil potential are, in general, slightly broader than those obtained with the KTTY potential. However, as no relativistic effects are included it is not possible to resolve the two D1 and D2 lines obtained in the experiment. Finally, for comparison, a cluster model, which is an approximation to the low, but non-zero temperature, has also been used and it has been found to be a simple yet good alternative, even if it is unable to estimate the line broadening directly.

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