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Spectral shift of sodium in a liquid-helium environment: A sequential Monte Carlo time-dependent density-functional-theory study

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The excitation lineshift and linewidth of the principal resonance line of Na embedded in liquid He have been obtained using combined Monte Carlo (MC) simulation and quantum mechanics (QM) calculations. The metropolis MC simulation used interatomic potentials obtained from high-level quantum mechanics results. Using the structures of the simulation statistically relevant configurations are sampled for subsequent QM calculations. The transition wavelengths for the $3s \rightarrow 3p$ principal resonance line of atomic Na were obtained using time-dependent density-functional-theory calculations of the central alkali-metal atom surrounded by the first solvation shell composed of 42 He atoms. The widths are obtained by the statistical distribution of calculated transitions. Three different functionals were used. Statistically converged results using the PBE1PBE/6-311++G(d,p) give a blueshift of 14.7 nm and a width at half maximum of 7.8 nm. Similar results are obtained using the Beeke-Lee-Yang-Parr three parameter exchange functional and the Becke three-parameter exchange with the Perdew nonlocal correlation functional models. These results seem to give a reasonable statistical representation of the structure of the He cavity enclosing the host Na atom and the consequent solvent effect on the $3s \rightarrow 3p$ excitation.

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I. INTRODUCTION

Spectral properties of foreign atoms and ions embedded in liquid helium have been the subject of intense experimental investigation in recent years. Understanding the spectral shift due to the interaction with the liquid helium environment is important because it gives a possible way of investigating different properties of the fluid using the foreign atoms as sensitive microprobes [1–4]. The interaction of the liquid helium with the guest atom modifies the spectral profile of the absorption band. Transition energies and line widths thus become important probes. With the recent advances in implantation techniques [5–8] a large number of different kinds of atoms have been the subject of the experimental investigation and a number of interesting observations on the spectral properties of the impurity atoms were made [9]. The implanted atom resides in a cavity inside liquid helium and the electronic density experiences a strong Pauli-type repulsion at the liquid helium boundary. The size of the cavity depends on the magnitude of the atom-helium interaction and is typically of the order of 6–12 Å in diameter, the shape depending on the angular momentum of the excitation [10–13]. Optical excitation of the central atom is expected to produce line shifts and broadening with respect to free atom due to the interaction with the host liquid environment. Although the spectra of alkali-metal atoms like Li, Na, and K attached to large helium clusters are available theoretically [14], experimental investigations failed to show the D lines in their recombination fluorescence spectra [6]. However, the excitation and emission spectra of neutral Rb and Cs are well established [8] and suggest an average blueshift of ~16 nm for the $5s \rightarrow 5p$ transition of Rb and a shift ~18 nm for the $6s \rightarrow 6p$ transition of Cs. Following this trend, for Na a slightly less shift of ca. 14–16 nm, would be expected. Recent theoretical estimates have obtained values of 16.7 nm [9] and 15 nm [14]. A large number of experimental data is available for alkali line shifts on liquid helium [1] but theoretical studies, in turn, are rather scarce. [9,14] One theoretical approach that has shown to be very useful is the standard bubble model (SBM). The SBM normally used for calculating such line shifts is based on evaluating first order energy changes in the ground and in the excited states using an average interaction potential. This average uses the density distribution of the liquid helium and some adjustable parameters. The model is approximate and in recent use has given only trends for the line shifts and underestimated the linewidths. [1]

A configuration coordinate analysis based on available pseudo-potential by Beau *et al.* [9] yields a blueshift of ~16.7 nm in the Na D line. Calculations based on the density functional theory [14] gives an average estimate of the blueshift of 15 nm for Na "D" excitation line. The purpose of the present work is to estimate the average line shifts in the excitation spectra of alkali atoms using an alternative and

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*Corresponding author. FAX: +55.11.3091-6831. Email address: ludwig@if.usp.br more realistic method, where the statistics of liquid systems is duly considered. As a liquid is composed of a collection of possible configurations with a given probability at a certain temperature all properties are to be obtained as an ensemble average. Hence, we study the excitation spectrum of Na in liquid He environment using a combination of Monte Carlo simulation and quantum mechanics. The configurations of the liquid are generated by computer simulation and structures are sampled for posterior use in QM calculations. This is a hybrid procedure termed as the sequential Monte Carlo/Quantum Mechanics methodology. [15–17] This S-MC/QM methodology has been successfully used before to describe solvatochromic shifts of organics molecules in different solvents. Also it has successfully described the transition energy and line shifts for the hydrated electron. [18] Essentially, configurations of the liquid environment around the Na atom are first obtained by Monte Carlo simulation. Next, the statistically relevant configurations are sampled for subsequent QM calculations of the entire system composed of the alkali atom and all He atoms within a certain solvation shell. This addresses first the problem of obtaining configurations of the He atoms surrounding the Na atom. Second, having performed the MC simulation, all the statistical information is available thus permitting an efficient protocol for the subsequent QM calculations. Only statistically relevant structures are used and all results reported are statistically converged. A relevant point of concern is that liquid He is a quantum fluid. To address this point we perform the MC simulation using two-body interatomic potentials derived from high-level *ab initio* quantum-chemical calculations. But it should also be noted that this model does not consider any contribution of the superfluid nature of the liquid. However, according to the experimental results [2] no spectral changes are observed in the optical spectra when the liquid goes through the phase transition from normal to superfluid liquid. That is, the spectral changes are insensitive when the liquid crosses the critical point of liquid helium. We are thus interested in incorporating the "solvent" field due to the helium atoms even if the detailed and complex He-He interaction is only approximate. Hence, a viable approximation worth analyzing is to describe the Na in liquid He using MC to generate the liquid configurations. One important aspect of the present treatment is that using the statistical distribution of calculated values one is able to describe the line broadening of the corresponding transition. The change of the alkali atom transition in the liquid. He environment involves not only the spectral shift of the absorption transition line but also the associated line broadening.

II. THEORETICAL METHODS

A. Monte Carlo simulation of Na in liquid helium environment

The theoretical determination of the structure of liquid helium is a complex theoretical problem. The basic interest here is to study the influence of the He environment in the spectral properties of alkali atoms, in special the case of Na. The MC simulation is performed using the standard Metropolis sampling technique [19]. We obtained the He-He pair potential using the coupled cluster [20] CCSD(T) with the high quality correlation-consistent cc-pV5Z basis set [21]. This is only an approximation to the very complex He-He dimer interaction [22–25]. For the Na-He interaction we used directly the van der Waals coefficients and potential depth due to Patil [26].

The Monte Carlo simulation has been done in the isothermal-isobaric NpT ensemble, where the number of He atoms N, its pressure p and temperature T were fixed. We used 1 Na and 1000 He atoms in the simulation. The pressure used was p=1 atm and the temperature is fixed ($T=2$ K) slightly below the transition temperature. The initial configurations were generated randomly and after a cooling procedure a thermalization stage of 5×10^6 MC steps is followed by an averaging stage of 24×10^6 steps. Every helium atom is thus attempted to move 24×10^3 times. The maximum allowed displacements of the atoms are auto-adjusted to give an acceptance rate around 50%. The radial distribution functions (RDF) are calculated to obtain information about the structure of He surrounding the Na atom.

In the subsequent QM calculations the Na excitation is calculated in the presence of all He atoms located in the first solvation shell. As we shall see this corresponds to 42 He atoms. The use of only the first shell is reasonable as it would be expected to dominate the theoretical description of the absorption spectra due to the weak polarization of the He atoms in the outer solvation shells. Computationally, it represents the explicit consideration of 95 electrons.

It is well known that successive configurations generated in the MC simulations, are statistically highly correlated, and will not give important additional information. Therefore we calculate the interval of statistical correlation using the auto-correlation function of the energy [15,16,27]. We only select configurations that give relevant statistical information [17,18,27,28]. Here we used the calculated auto-correlation function [15,27] of the energy to extract 50 configurations, with less than 15% of statistical correlation. These configurations will be submitted to the QM calculations. As we shall see this is enough to obtain statistically converged results for the transition energies. The MC simulation and the necessary QM interface have been performed using the DICE [29] program.

B. Quantum mechanics calculations

The structures of the Na atom in the liquid He environment, obtained from MC simulations, were submitted to QM calculations. As discussed in the previous section, a total of 50 configurations, composed of the central Na and the 42 He atoms in the first solvation shell, were separated from the MC simulation for the QM calculations. All atoms are explicitly included in the QM calculations. No distinction is made between the electrons in the reference Na atom and in the environmental He atoms. Clearly, some compromise is necessary for the calculation of the absorption spectrum. We have hence used the time-dependent DFT (TD-DFT) level in the hybrid functional of Perdew, Burke, and Ernzerhof (PBE1PBE) [30]. In addition to verify the performance of

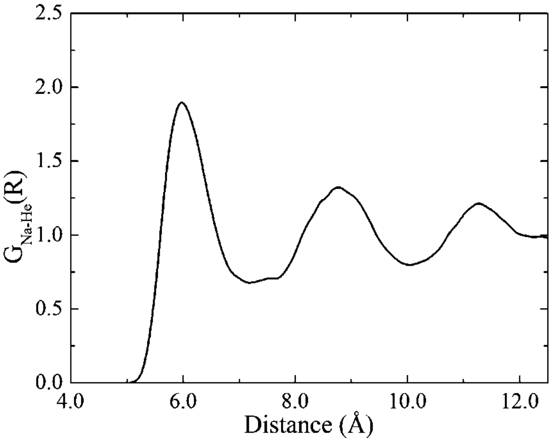

FIG. 1. Pairwise radial distribution functions between Na and He.

other functionals we used the three-parameter exchange correlation functional of Becke-Lee-Yang and Parr (B3LYP) [31,32] and the three-parameter exchange B3 with the Perdew nonlocal correlation functional(B3P86) [33]. The three functionals are of the generalized gradient (GGA) type. The calculations were made using localized Gaussian-type basis functions 6-311++G(d,p) for the Na-He_n system. This basis includes both diffuse and polarization functions in the He and Na atoms. This is a good computational compromise corresponding to a total of 324 basis functions for the Na and all 42 He atoms. For the isolated Na atom this gives transition energies that are slightly larger than experiment but we focus here on transition energy shifts. Additionally the correlated basis cc-pVTZ was also used in combination with the B3LYP density functional. This leads now to a total of 622 basis functions for the Na plus 42 He atoms. All QM calculations were made using the Gaussian 03 program [34].

III. RESULTS AND DISCUSSIONS

We first discuss the structural aspects regarding the distribution of He around the Na atom. Figure 1 shows the calculated RDF between the Na and the He atoms derived from the MC simulation. As it can be seen the He atoms are well structured around the central Na atom and three solvation shells are easily discernible. The first solvation shell starts at 5.1 Å and ends at 7.1 Å with a pronounced maximum at 5.9 Å. The spherical integration of this first peak gives the coordination number, or the number of the nearest He atoms around the Na atom. Our calculation gives an average number of 42 He atoms in this first solvation shell. There is no possibility at present to make a direct comparison of the structure of He around Na. In fact, we cannot discard the possibility that quantum effects, not included here, will affect the Na-He radial distribution function. However, there is indirect theoretical information that corroborates the feasibility of the calculated structure. In fact, an increase of the density of the He atoms at 5 Å away form the central Na atom has been obtained by De Toffol *et al.* [14]. Also a recent theoretical work [35] based on path integral Monte Carlo has obtained an increase of the density on a distance of approximately 5 Å from the central Na atom. These results suggest that the structural aspects obtained here are in line with previous theoretical studies and will be used in the forthcoming QM calculations. The number of He atoms in the first coordination shell cannot be assured without explicit consideration of quantum effects. But we take the present results of the MC simulation as a reasonable statistical approximation.

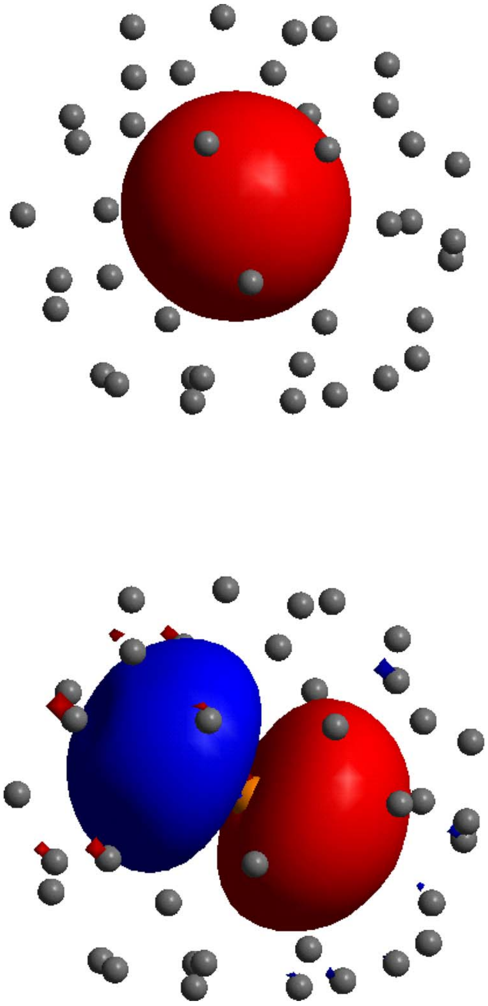

FIG. 2. (Color online) The *s*- and *p*-type orbitals of the Na atom surrounded by the first solvation shell composed of 42 He atoms.

The $3s \rightarrow 3p$ excitation energies of the Na atom in the He environment were calculated using the configurations generated by the MC simulation, as described above. Figure 2 shows one representative configuration with the s- and p-type orbitals of Na in the He liquid environment. Note that these orbitals are localized in the Na atomic center. The calculated transition energies are represented by a distribution of values. The histogram, and the corresponding gaussian distribution, of calculated transition energies using the PBE1PBE/6-311++G(d,p) model and is shown in Fig. 3. Of course in the environment, opposite to the gas phase situation, the degeneracy of the p-type orbital is broken. Hence, there are three closely located $3s \rightarrow 3p$ excitation for each Na-He_n structure used. Note that opposite to the molecular case where vibration can contribute to the line broadening for this atomic calculation here the line broadening reflects

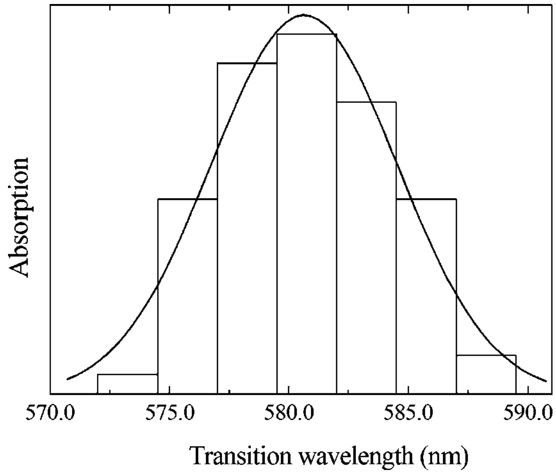

FIG. 3. Histogram with Gaussian convolution for the *s*-*p* absorption transition of Na in liquid He environment. Results obtained with PBE1PBE/6-311++G(*d*,*p*).

the statistical distribution of configurations. As can be seen in Fig. 3 the maximum of the spectral distribution calculated with the PBE1PBE is located at 580.7 nm. This leads to a blueshift of 14.7 nm compared to the gas phase value obtained at 595.4 nm. This blue shift result is in good agreement with previous theoretical results [9,14] and the expected experimental [8] trend. The results obtained for the other functionals are also reported in Table I. Whereas the PBE1PBE gives the blueshift of 14.7 nm the other cases give a slightly larger shift, in the range of 18.6 to 18.9 nm. For instance, a shift of 18.9 nm is calculated for the B3LYP/6-311++G(d,p) model. As expected and observed in other alkali systems the absorption presents a broad linewidth. Our values presented in Table I show widths at half maximum of 5.0 to 6.6 nm for the theoretical models here considered. The width at half maximum is obtained here as 7.8 nm for the PBE1PBE and around 6 nm for the B3LYP and B3P86 models. Apparently there has not been a previous attempt to obtain the line width of Na in He. However experimental results [8] are available for Rb and Cs, where the widths are in the range of 4 nm and 8 nm. This indicates that the present theoretical results are in reasonable agreement. In the present study the width is directly obtained from the statistical distribution of calculated results. Table I also compares our results with other previous theoretical values. Theoretical values for the transition energy shifts were reported previously. Beau *et al.* [9] using a combination of tunneling model and pseudo-potential approach has obtained that the center of the absorption line in the case of Na is blueshifted by 16.7 nm. A blueshift of approximately 15 nm has been obtained by De Toffol *et al.* [14] using a DFT approach. Overall, there is a general agreement between all the theoretical results but in the present calculations the use of PBE1PBE seems to give a better representation of the blueshift. The advantage of the present methodology lies in that the transition broadening is naturally obtained from the statistical distribution. Also it gives an approximate description of the structure of the liquid He cavity that encloses the host atom.

TABLE I. Calculated transition shifts and widths at half maximum (in nm) for Na atom in liquid helium environment.

	Transition shifts (nm)	Width (nm)
Ref. [9]	16.7	
Ref. [14]	15.0	
PBE1PBE/6-311++G(*d*,*p*)	14.7±0.3	7.8
B3LYP/6-311++G(*d*,*p*)	18.9±0.3	6.1
B3P86/6-311++G(*d*,*p*)	18.1±0.3	6.2
B3LYP/cc-pVTZ	18.6±0.3	6.4

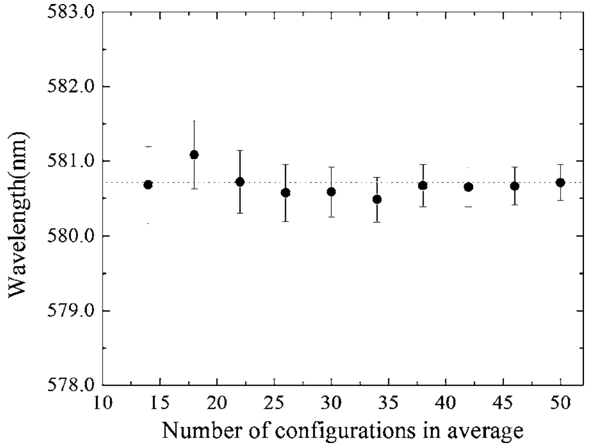

FIG. 4. Statistical convergence of the absorption transition wavelength of the *s*-*p* line of Na in liquid He environment. Results obtained with PBE1PBE/6-311++G(*d*,*p*).

The calculated values of the absorption spectra are derived from several quantum mechanical TD-DFT calculations using the Na-He$_n$ structures sampled from the simulation. To analyze the statistical convergence Fig. 4 shows the calculated transition wavelengths using the PBE1PBE/6-311++G(*d*,*p*) model. As can be seen converged results are obtained already for 40 TD-DFT calculations. The fast convergence is an outcome of using statistically uncorrelated configurations. [27] The statistically converged result leads to a blue shift of 14.7 nm compared to the corresponding transition in the gas phase.

IV. SUMMARY AND CONCLUSIONS

The absorption spectra of the Na atom in liquid He environment were obtained using a combination of Monte Carlo simulation and Quantum Mechanics time-dependent DFT. In spite of the approximate atomic interactions the essential aspects of the absorption spectrum were obtained. TD-DFT calculations were performed in the structures composed of the Na atom surrounded by the first solvation shell of He, generated by Monte Carlo simulations. The calculated average blue shift of 14.7 nm, obtained with the PBE1PBE functional is in line with earlier calculated values and the expected result from the experimental trend. The use of the B3LYP and B3P86 functionals gave blue shift values in the range of 18.5 nm which are perhaps slightly larger by

~2–4 nm from the expected experimental result. The calculated line widths range between 6 and 8 nm and are all within the experimental expectations as judged from the available results obtained for the other alkali atoms. The importance of the statistical distribution is emphasized and the calculated average transition energy values are statistically converged. Finally, the present results seem to corroborate that this model combining quantum and statistical mechanics is promising for the description of alkali atoms in He liquid environment. In the case considered here it gives a reasonable statistical representation of the structure of the He cavity enclosing the host Na atom and the consequent solvent effect on the $3s \rightarrow 3p$ excitation.

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