Combining Monte Carlo simulation and density-functional theory to describe the spectral changes of Na_2 in liquid helium

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Spectral changes of Na_2 in liquid helium were studied using the sequential Monte Carlo–quantum mechanics method. Configurations composed by Na_2 surrounded by explicit helium atoms sampled from the Monte Carlo simulation were submitted to time-dependent density-functional theory calculations of the electronic absorption spectrum using different functionals. Attention is given to both line shift and line broadening. The Perdew, Burke, and Ernzerhof (PBE1PBE, also known as PBE0) functional, with the PBE1PBE/6-311++G(2*d*,2*p*) basis set, gives the spectral shift, compared to gas phase, of 500 cm^{-1} for the allowed $X\,^1\Sigma_g^+ \rightarrow B\,^1\Pi_u$ transition, in very good agreement with the experimental value (700 cm^{-1}). For comparison, cluster calculations were also performed and the first $X\,^1\Sigma_g^+ \rightarrow A\,^1\Sigma_u^+$ transition was also considered.

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I. INTRODUCTION

Liquid helium is one of the most intriguing systems exhibiting properties of enormous physical interest [1]. In more recent years an additional focus of interest has been directed to the properties of foreign atoms in a liquid-helium environment [2–40]. The presence of the liquid helium in the surrounding modifies the free atomic potential leading to spectral changes both in the transition wavelengths and line profile. Thus foreign atoms can act as interesting microprobes for analyzing the helium properties. The studies of foreign atoms in liquid helium have considerably increased because of the recent advances in implantation techniques (see Ref. [40]). Although a large number of experimental data are available for atomic line shifts on liquid helium [2–40], theoretical investigations are still scarce [9,41–50]. A recent survey of theoretical studies has been published [51]. It is known that due to the Pauli repulsion the implanted atom resides in a large cavity inside liquid helium. The size and shape of the cavity depend on the impurity and they change following the magnitude of the impurity-helium interaction. These are typically of the order of 8–12 Å in diameter but the free electron in bulk helium attains the very large diameter of ∼34 Å [40,52]. This is the support for the standard bubble model [5,40,46–49] used for calculating these line shifts. This is a useful but limited approximate method that normally gives only trends for line shifts and widths [5,51]. An additional procedure is the use of cluster models where the impurity is surrounded by a few helium atoms, normally located in a spherical distribution [43–45]. In this case explicit environment atoms are included but their positioning is somewhat arbitrary and fixed. The number and location of the helium atoms can be determined by the density of the system and relatively good results can be obtained for the spectral shift. Because only one structure is normally used the temperature, and related inhomogeneous effects, are not considered.

An interesting alternative is provided by the combined use of liquid simulation and quantum mechanics (QM) [42]. In this case, the liquid simulation is used to provide representative configurations of the system whereas subsequent QM calculations can obtain the spectral characteristics. This is used in this work for describing the spectral changes of Na_2 in liquid helium. Several theoretical studies have been directed to alkali-metal atoms and other simple atoms in bulk liquid helium but molecules have not been considered. One possible reason is that most experiments are done for these alkali-metal atoms and few results are known for molecules, although these have been considered in helium droplets [40,53–55]. Our work has been directed to the description of foreign atoms and molecules in bulk liquid helium but important theoretical developments are underway also for describing molecules in helium droplets [56]. Na_2 is a challenging case [22] where the spectral blueshift in liquid helium is only 700 cm^{-1} (16 nm) compared to the free molecule. It is important to mention that it has been seen experimentally [2] that the spectral changes of atoms are insensitive when the temperature of the system crosses the λ point. This is assumed to be the case also for Na_2.

In this work Monte Carlo (MC) simulations and QM calculations are performed for the Na_2 molecule in liquid helium. The results reported are converged both with respect to the statistics as well as the size of the systems (i.e., number of explicit environment atoms used). An attempt is also made to give a characterization of the cavity (the bubble) where the molecules reside. In addition, attention is given to the inhomogeneous broadening of the absorption band.

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II. THEORETICAL METHODOLOGY

To generate the structure of helium around Na_2, Metropolis MC simulations using the Lennard-Jones potential are performed in the *NPT* ensemble. We adopt the He-He potential used successfully in a previous study [42] of atomic Na in liquid helium. Similarly [42] for the Na-He we adopt the potential derived by Patil [57]. In the simulations the Na-Na distance is kept fixed at the experimental equilibrium distance of 3.079 Å [58]. In the MC simulation we used 1 Na_2 and 999 He atoms. The temperature is fixed at $T = 3$ K, above the superfluid transition temperature, and the pressure is fixed at $P = 1$ atm. The sampling of the configurations is made after obtaining the autocorrelation function of the energy [59,60]. As it will be seen the first solvation shell comprises 54 He atoms that will be treated explicitly, composing a supersystem with 130 electrons. The wave function of the (Na_2 + 54 He) system is antisymmetric with respect to all electrons, thus including the important Pauli exchange interaction.

The calculations of the spectrum have been performed with the time-dependent density-functional theory (TDDFT) using different parametrizations for the exchange-correlation. These will include the three-parameter exchange-correlation functional of Becke-Lee-Yang and Parr (B3LYP) [61,62] and in addition we have also used the Handy-Cohen exchange in the LYP correlation, the so-called O3LYP [63], and Perdew, Burke, and Ernzerhof (PBE1PBE, also known as PBE0) [64]. The calculations were made using different Gaussian-type basis functions that will be mentioned along with the results. For Na we have used several basis sets such as 6-311++G(2*d*,2*p*), the quadruple zeta valence quality (def2-qzvp) of Weigend and Ahlrich [65], and the basis set devised by Sadlej [66]. Different basis sets have been used for the helium atoms but we will mostly report the results we have obtained using the 6-311++G(2*d*,2*p*) basis. The MC simulation and the necessary QM interface have been performed using the DICE program [67] and all QM calculations were performed using the GAUSSIAN 03 program [68].

III. RESULTS AND DISCUSSIONS

A. The coordination of Na_2 in liquid helium

The coordination of helium atoms around the central Na_2 molecule is determined by the radial distribution function (RDF). Figure 1 shows the RDF between the center of mass of Na_2 and the helium atoms. Several solvation shells are discernible. The first maximum corresponding to the first solvation shell is the one of maximum interest. As it can be seen this first solvation shell starts at 5.1 Å and ends at 8.0 Å, having a maximum at 6.9 Å, comprising a total of 54 helium atoms. This is then the size of the supersystem, composed of one Na_2 molecule surrounded by 54 helium atoms that will be submitted to QM calculations of the electronic spectrum. Figure 2 shows the Na_2 inside the cavity formed in liquid helium. Helium atoms are located from a distance of 5.1 Å to the center of mass of Na_2, but the first maximum of the distribution is located slightly further from this point, at 6.9 Å. The cavity thus has a diameter of 10.2 Å. Figure 2 gives a good visualization of the size and shape of the cavity (useful in the bubble model). It is worthwhile to note that

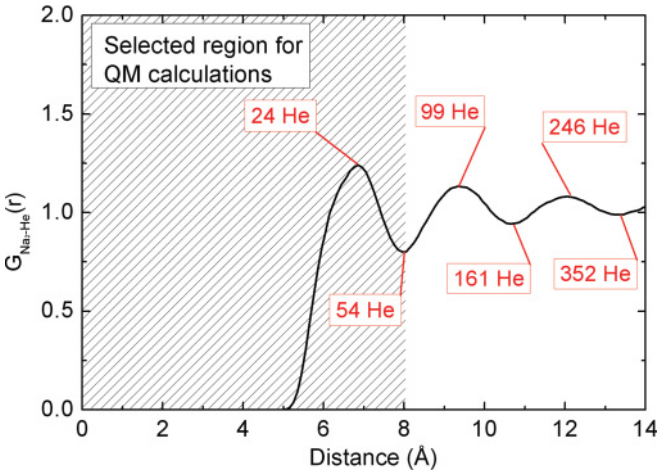

FIG. 1. (Color online) Radial distribution function between the center of mass of Na_2 and helium atoms.

the interaction of Na dimer with the surrounding liquid He atoms is slightly different than the atomic Na interaction in liquid He resulting [42] in different positions of the maximum of the first solvation shell and the number of He atoms in the respective cases. In the atomic Na the first solvation shell comprises a total of 42 helium atoms with the same cavity radius of 5.1 Å [42]. Aside from the different symmetry of the cavity one important distinction is the position of the first maximum in the density. In the atomic case it is 1.0 Å shorter; i.e., 5.9 Å. The change in symmetry along and perpendicular to the dimer axis is small (because of the nature of the highest occupied molecular orbital in the dimer) but can also be seen in Fig. 2.

The first two low-lying electronic excitations of Na_2 are characterized by the promotion $4\sigma_g \rightarrow 4\sigma_u$ and $4\sigma_g \rightarrow 2\pi_u$ giving rise to the two low-lying excited states $A\,^1\Sigma_u^+$ and $B\,^1\Pi_u$, respectively. The lowest lying transition $X\,^1\Sigma_g^+ \rightarrow A\,^1\Sigma_u^+$ is located in the region of 680 nm and has not been observed in the liquid-helium experiments [22]. The

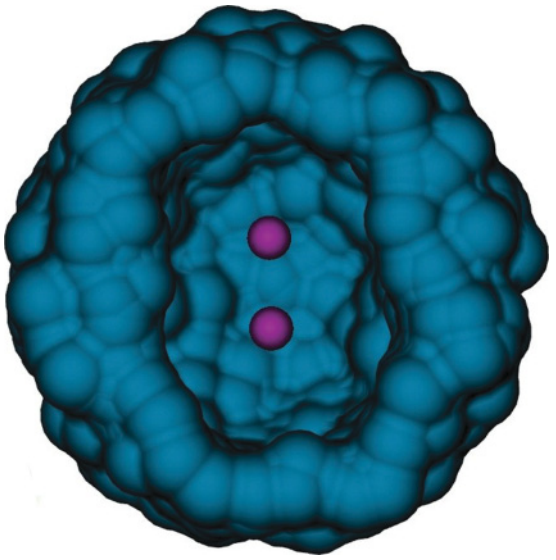

FIG. 2. (Color online) Superposition of the MC configurations of helium atoms around the Na_2 molecule.

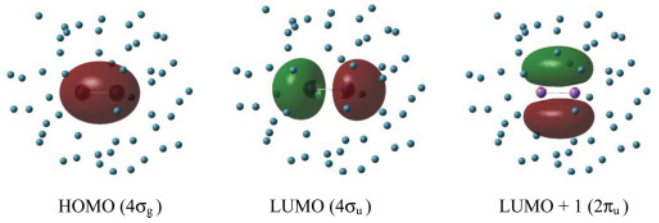

FIG. 3. (Color online) Calculated molecular orbitals involved in the low-lying excitation of Na_2.

$X\,^1\Sigma_g^+ \rightarrow B\,^1\Pi_u$ transition is the symmetry-allowed band experimentally detected in the region 450–500 nm. This second $B\,^1\Pi_u$ excited singlet state shifts toward the blue side of the spectrum when Na_2 is implanted in the liquid-helium environment, corresponding to an experimentally detected shift [22] of 700 cm^{-1}. The first excited $A\,^1\Sigma_u^+$ singlet state, although not detected in the helium environment, may have a role to play in the emission after the excitation to the $B\,^1\Pi_u$ state [22]. Figure 3 shows the molecular orbitals involved in the excitation of Na_2 for the situation in liquid helium. As it can be seen most of the characteristics of the free molecular orbitals are preserved in the liquid environment and this is because of the weak interaction between the implanted molecule and the helium atoms. However, as expected the $2\pi_u$ orbital will break the symmetry due to the environment and this will contribute also to the broadening of the absorption band.

B. Spectral changes of Na_2 in liquid helium

One-hundred statistically uncorrelated configurations were sampled and submitted to the calculation of the absorption spectrum. As normal, we assume the Franck-Condon approximation and the Na-Na distance is kept fixed in the excitation. The results are shown in Table I. Every entry in this table is the result of the average excitation energy. Results obtained using the B3LYP functional were in general too high. For instance, using the 6-311++G(2*d*,2*p*) for all atoms we obtained a calculated shift of 1010 cm^{-1}, compared with the experimental result of 700 cm^{-1}. In opposition, the other two functionals led to results that are slightly underestimated, ranging between 400 and 550 cm^{-1}. As in a previous study on the spectral shift of a Na atom in liquid helium [42] we find that the PBE1PBE functional seems to give the best balanced result for the spectral shift. Given the small magnitude of the shift (ca. 16 nm or 0.09 eV) we could conclude that both the O3LYP and PBE1PBE models give very good results, ranging between 405 and 550 cm^{-1}. One interesting aspect that distinguishes the explicit liquid model from a cluster model, or any model that uses a fixed configuration, is the possibility of describing the inhomogeneous broadening in the absorption transition. This has not been explicitly reported in the experiments. But analysis of the absorption band [22] allows a reasonably good estimate. At half maximum the full band ranges between ca. 462 and 476 nm, thus giving an experimental half width at half maximum close to 300 cm^{-1}. At least three contributions can be discerned for the linewidth. There is a splitting of the degenerate $2\pi_u$ orbital, the configuration effect leading to inhomogeneous broadening and the change in the geometry of the excited state (leading to overlap Franck-Condon factors). Only the first two are considered here as they are directly obtained from the statistical distribution. Table I thus also reports the calculated half-widths for the observed *B* band. A good description is obtained with the O3LYP model. In particular, using the 6-311++G(2*d*,2*p*) basis set a very good result of 250 cm^{-1} is obtained for the half-width. Overall the PBE1PBE/6-311++G(2*d*,2*p*) and O3LYP-sadlej models emerge as the two best models adopted here.

Before concluding this section there is the natural question of whether the use of 54 explicit helium atoms is enough to achieve convergence. Although this is to be expected because of the weak Na-He and He-He interactions it is still of interest,

TABLE I. Calculated transition blueshift (in cm^{-1}) for Na_2 in a liquid-helium environment. Results are averages over 100 QM calculations on structures composed by one Na_2 molecule surrounded by 54 explicit He atoms. In parenthesis are shown the calculated half-width at half maximum and comparison with the estimated experimental value.

		Transition blueshift (cm^{-1})	
Model	Basis set (Na)	$X\,^1\Sigma_g^+ \rightarrow A\,X\,^1\Sigma_u^+$	$X\,^1\Sigma_g^+ \rightarrow B\,^1\Pi_u$
PBE1PBE[a]	6-311++G(*d*,*p*)	80	550(140)
O3LYP[a]	6-311++G(*d*,*p*)	150	495(255)
B3LYP[a]	6-311++G(*d*,*p*)	320	1080(160)
PBE1PBE[b]	6-311++G(2*d*,2*p*)	40	500(135)
O3LYP[b]	6-311++G(2*d*,2*p*)	85	425(250)
B3LYP[b]	6-311++G(2*d*,2*p*)	270	1010(155)
PBE1PBE[b]	def2-qzvp	30	435(130)
O3LYP[b]	def2-qzvp	75	405(215)
B3LYP[b]	def2-qzvp	265	910(150)
PBE1PBE[b]	sadlej	45	505(135)
O3LYP[b]	sadlej	50	450(230)
B3LYP[b]	sadlej	270	1020(155)
PBE1PBE[b]	aug-cc-pVQZ	20	490(135)
Experiment [22]		–	700(300)

[a]Basis set for He is 6-311++G(*d*,*p*).
[b]Basis set for He is 6-311++G(2*d*,2*p*).

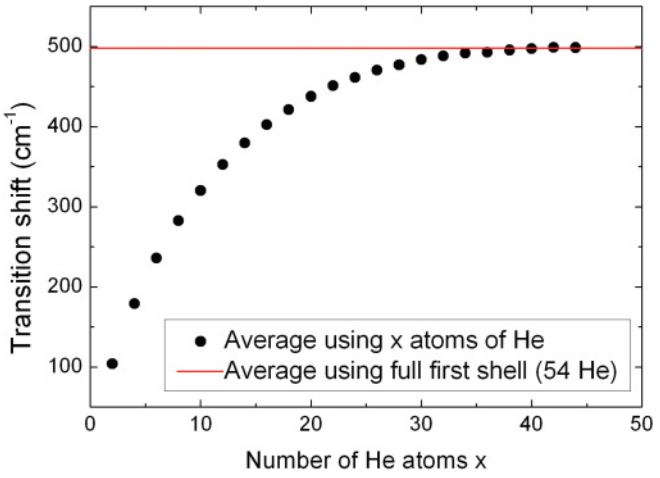

FIG. 4. (Color online) Convergence of the calculated transition-energy shifts with the number of helium atoms explicitly included in the QM calculation. Every entry is the result of an average excitation energy obtained with 100 quantum-mechanical calculations. Results obtained with the PBE1PBE/6-311-G(2*d*,2*p*) model.

in particular to assure the point of convergence. Figure 4 shows the calculation of the spectral shift with an increased number of helium atoms being used. Every point in Fig. 4 is the result of an average over 100 configurations composed of Na_2 and x atoms of helium. We note that convergence is obtained for $x \approx 35$ helium atoms. This demonstrates the convergence of our results with respect to the number of explicit helium atoms used here. But it also emphasizes that this convergence only comes after including all atoms up to a distance of ca. 7.5 Å from the center-of-mass of the Na_2 molecule. This value may seem surprisingly large because of the weak Na-He interaction.

C. Spectral changes of Na_2 in a cluster of helium atoms

For low-temperature systems, such as the case of liquid helium, the temperature effects are expected to be small, although they have never been discerned. Several previous theoretical studies of the spectral changes of alkali-metal atoms in liquid helium have relied on clusters calculations with a limited number of atoms to represent the environment. The position of the environmental atoms are determined either by geometry optimization, which means a maximization of the Na_2-He interaction, or by the density [43,69]. In view of some recent results [43], this seems to be a reasonably good model even if it cannot be used for determination of the line broadening. We now discuss our results obtained using a cluster calculation with 14 helium atoms in a spherical distribution equally separated from the center of mass of the Na_2. The distance R between the center of mass of Na_2 and any He atom has been optimized in the different QM models adopted. Eight helium atoms are placed in the vertices of a cube and the remaining six atoms are placed above the center of the cube faces but all He atoms are separated from Na_2 by R_{opt}. Table II shows the calculated distances for every DFT model. As expected these distances are shorter than the corresponding distance in the liquid case, obtained from the distribution function (Fig. 1). For instance, whereas in the liquid case one obtains a maximum in the distribution at 6.9 Å, in the optimized cases the R_{opt} distance is always smaller and the PBE1PBE/6-311++G(2*d*,2*p*) model, for instance, obtains an optimal distance of 5.8 Å. This is, however, relatively close to the beginning of the distribution of helium atoms (5.1 Å) and more closely to the effective bubble radius ~6 Å. The corresponding calculated shift for the second $B\,^1\Pi_u$ excited singlet state is now 470 cm^{-1}, also in good agreement with experiment. Comparing with the results shown in Fig 4, where the calculated shift for 14 helium atoms in the liquid case gives the value of 380 cm^{-1}, it is clear that the good agreement with experiment is a consequence of small error cancellation. Indeed, comparing with the more realistic converged MC-QM results the use of a limited number of environmental helium atoms decreases the calculated shift (Fig. 4) but using optimized Na-He distances maximizes the interaction leading to an increase in the calculated shift. The geometry optimization seems to have a larger impact in the first singlet absorption, the $A\,^1\Sigma_u^+$ band. In this case all transition energy shifts are larger than the corresponding ones in liquid helium.

IV. SUMMARY AND CONCLUSIONS

The changes in the absorption spectrum of the Na_2 molecule in a liquid-helium environment were studied using a realistic model for incorporating temperature effects. Experimental results are available only for the second excitation, the $X\,^1\Sigma_g^+ \rightarrow B\,^1\Pi_u$ transition, and give an absorption blueshift of 700 cm^{-1} compared to the free molecule. A good description of the shift is obtained combining Monte Carlo simulation and TDDFT quantum-mechanics calculations. The exchange interaction is

TABLE II. Calculated transition blueshift (in cm^{-1}) for Na_2 in liquid-helium environment obtained with the PBE1PBE functional. Basis set for He is 6-311++G(2*d*,2*p*). Results are obtained using the cluster model with one Na_2 surrounded by 14 explicit He atoms, located at minimum energy distances that are also shown. See text.

		Transition blueshift (cm^{-1})	
Basis set (Na)	R_{opt} (Å)	$X\,^1\Sigma_g^+ \rightarrow A\,X\,^1\Sigma_u^+$	$X\,^1\Sigma_g^+ \rightarrow B\,^1\Pi_u$
6-311++G(2*d*,2*p*)	5.77	505	470
aug-cc-pVQZ	5.77	495	450
def2-qzvp	5.79	475	405
sadlej	5.73	550	490
Experiment [22]		–	700

explicitly included by the antisymmetrization of the wave function including the foreign system and the environment atoms. The PBE1PBE/6-311++G(2*d*,2*p*) model obtained a shift of 500 cm^{-1}, in good agreement with the experimental results. This value for the shift is obtained using one Na_2 surrounded by 54 explicit He atoms and is the average of 100 configurations. This is verified to be statistically converged and also converged with respect to the number of helium atoms explicitly included in the system. Some considerations are also given for the line broadening and the experimental half-width at half maximum is well reproduced. We consider here the contributions originating from the splitting of the $B\,^1\Pi_u$ state in the liquid environment and the temperature effects included in the different configurations sampled from the simulation. No attempt has been made to obtain the contribution originating from the Franck-Condon factors. Similar considerations have been made for the lowest and undetected $X\,^1\Sigma_g^+ \rightarrow A\,^1\Sigma_u^+$ absorption transition. Finally, for comparison, an optimized cluster model has been used and seen to give reasonably good results albeit using only a limited number of explicit helium atoms.

ACKNOWLEDGMENT

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