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REGULAR ARTICLE

Spectroscopy of sodium atom in liquid helium cluster: a symmetry adapted cluster-configuration interaction (SAC-CI) study

B. Saha · R. Fukuda · H. Nakatsuji · P. K. Mukherjee

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Abstract Excitation line shift of the principal resonance line of sodium atom embedded in liquid helium is estimated using symmetry adapted cluster-configuration interaction (SAC-CI) method with a reasonably good choice of basis set. The effect of the liquid surroundings is considered by taking only the nearest neighbor interaction using several model clusters of helium atoms with a centrally located isolated sodium atom. The transition wavelength of the $^2P \leftarrow {}^2S$ line of Na is estimated both for the free Na and for the Na atom centrally located inside a model helium cluster. The shift depends obviously on the model cluster and the distance of the central Na atom from the surrounding He atom. With a physically realizable structure, SAC-CI calculation correctly predicts the theoretical results obtained previously on such estimates.

Keywords Spectral shift · Helium cluster · SAC-CI calculations

1 Introduction

In recent years extensive experimental investigations were done for finding the spectral properties of foreign atoms and ions embedded in liquid helium. On one hand the experiments furnish various changes in the structural properties of the implanted foreign atoms and on the other hand, they provide possible ways of investigating the properties of the quantum fluid using the foreign atoms as sensitive microprobes [1–4]. As a consequence of the surrounding helium atoms the free atomic potential is modified, and the transition wavelength and the line profiles are altered. Recent advances in the implantation techniques [5,6] have made it possible to investigate a large number of atoms experimentally and several interesting structural properties of the impurity atoms have been found [7]. The implanted atom resides in a cavity, the form of which depends on the central atomic structure, the size being determined by the impurity-helium interaction and typically ∼8 to 12 Å in diameter [8–11]. The radius of this cavity is called bubble radius (r). The wave function of the central impurity atom experiences a strong Pauli-type repulsion at the liquid helium boundary. Although the spectra of light alkali atoms like Li, Na and K attached to helium nano bubbles are available [12], experiments fail to show the resonance lines in their recombination fluorescence spectra [5]. Theoretical estimations are, however, available for the shift in the principal ‘D’ line of Na atom. A configuration co-ordinate analysis based on available pseudo potential between Na and He atom by Beau et al. [7] yields a blue shift of ∼16.7 nm whereas a density functional analysis by Toffol et al. [12] furnishes an estimate of 15 nm blue shift for the Na ‘D’ excitation line. A sequential Monte Carlo time dependent density functional calculation on the principal resonance line of Na embedded in liquid helium according to Ludwig et al. [13] yields a blue shift of ∼14.7 nm which is in reasonable agreement with the very few available data. The number of theoretical calculations along this line is rather scanty [1], although experimental observations for the higher alkali atoms like Rb and Cs are well established now, the shifts being predicted as ∼16 and 18 nm, respectively [14].

B. Saha · R. Fukuda · H. Nakatsuji
Department of Synthetic Chemistry and Biological Chemistry,
Kyoto University, Katsura, Nishikyo-ku,
Kyoto 615-851, Japan

P. K. Mukherjee (✉)
Department of Spectroscopy,
Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700-032, India
e-mail: sppkm@iacs.res.in

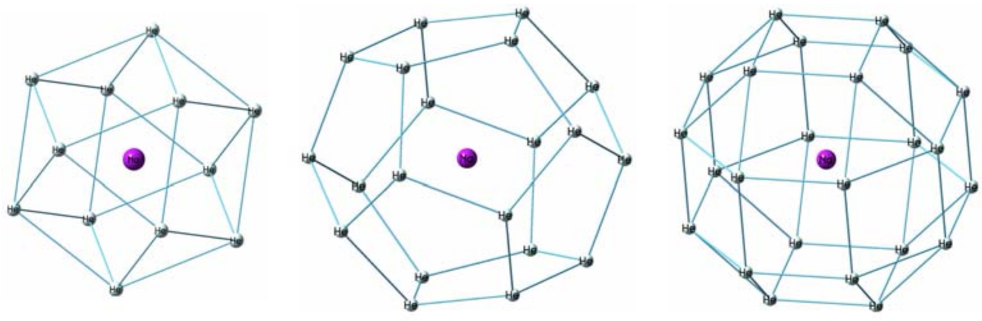

Na-He$_{12}$ Na-He$_{20}$ Na-He$_{24}$

Fig. 1 Schematic representation of Na–He$_n$ cluster of radius 7 Å. Na—*violet* (dark), He—*pale blue* (light). He-atoms are connected to show the shape of the cluster

The purpose of the current note is to understand and estimate the effect of surrounding helium cluster on a centrally located alkali atom from a standpoint which uses ab-initio quantum chemical methods. The Na atom is chosen as the impurity as this is not too large a system to be tackled using ab-initio methods and for which estimate the spectral line shift is available [7,12,13]. The methodology we have adopted is the symmetry adapted cluster-configuration interaction (SAC-CI) which has been well tested on studying the excitations from various extended systems [15–21]. We take the possibility of distributing the surrounding helium atoms in different shells, the structures of which are determined by inter-atomic forces. Because of strong Pauli repulsion, the non-nearest shells are expected to produce a very small effect on energy levels, and we consider the interaction of the central Na atom with the nearest neighbor shell, the radius of which is determined by the Na–He interaction potential, and the number of helium atoms in the first shell is determined by our specific model.

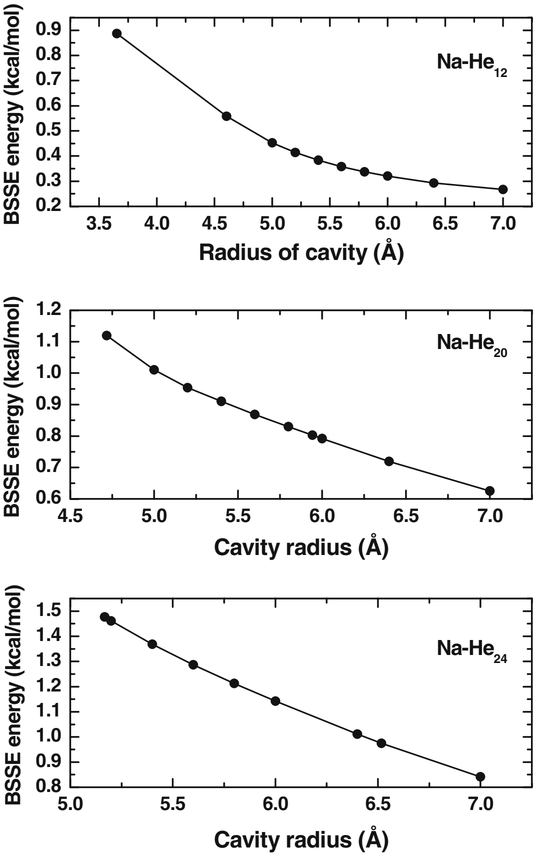


Fig. 2 Basis set superposition error (BSSE) energy (correction to total interaction energy) against cavity radius for different Na–He$_n$ clusters

In a cluster calculation the following two points has to be considered

1. The Na–He distance in the cluster must be in conformity with the inter-atomic distances between Na and He diatomic systems. A reasonable estimation given by Ancillito et al. [9] is ~6.06 Å. It is also noted from their calculation [9] that in presence of surrounding He cluster the distance diminishes and the estimate is ~ 5.05 to 5.06 Å.
2. The He–He distance in the cluster should be more or less compatible to the He–He inter-atomic distance. Ab initio calculations yield He–He distance as ~3 Å. While at normal liquid helium density of 0.0218 Å^{-3}, the result obtained from a closed pack plane of He atoms [11] yields a distance ~4 Å.

2 Computational details

Hence, whatever may be the model cluster, for the realistic description one has to incorporate the above two points. We performed calculations with three different cluster configurations Na–He$_{12}$, Na–He$_{20}$ and Na–He$_{24}$. For the Na–He$_{12}$

Table 1 Transition wavelength of the $^2P \leftarrow {}^2S$ resonance line for different Na–He$_n$ clusters computed using SAC-CI method

Cavity radius (Å)	He–He distance (Å)	λ_{LHe}(Å)	$\Delta\lambda = \lambda_{free} - \lambda_{LHe}$ (Å)	f_{LHe}
Na–He$_{12}$				
7.0	9.8995	5964	4	0.3368
6.4	9.0510	5925	43	0.3374
6.0	8.4853	5879	89	0.3375
5.8	8.2024	5846	122	0.3374
5.6	7.9196	5807	161	0.3372
5.4	7.6368	5758	210	0.3367
5.2	7.3540	5699	269	0.3359
5.0	7.0711	5630	339	0.3346
4.6038[a]	6.5107	5450	518	0.3306
3.6540[b]	5.1676	4843	1125	0.2892
Na–He$_{20}$				
7.0	4.9955	5946	22	0.3284
6.4	4.5673	5889	79	0.3390
6.0	4.2819	5815	153	0.3388
5.8	4.1391	5769	199	0.3388
5.6	3.9964	5710	258	0.3384
5.4	3.8537	5632	336	0.3294
5.2	3.7110	5550	418	0.3366
5.0	3.5682	5448	520	0.3351
5.9434[a]	4.2415	5802	166	0.3311
4.7173[b]	3.3665	5275	693	0.3320
Na–He$_{24}$				
7.0	5.0037	5929	39	0.3377
6.4	4.5748	5859	109	0.3386
6.0	4.2889	5779	189	0.3387
5.8	4.1459	5723	245	0.3384
5.6	4.0030	5655	313	0.3379
5.4	3.8600	5573	395	0.3371
5.2	3.7170	5477	491	0.3358
6.5172[a]	4.6586	5877	91	0.3385
5.1676[b]	3.6938	5460	508	0.3356

Basis set used for Na and He atoms are 6s5p3d1f + s(d) + p(d) and 5s + 1s(d), respectively. For isolated Na atom $\lambda_{free} = 5968$ Å

[a] n(He) = 0.0109 Å^{-3} (Number density of He at half bulk density)

[b] n(He) = 0.0218 Å^{-3} (Number density of liquid ^{4}He)

cluster we used regular icosahedral model and for Na–He$_{20}$ we used regular dodecahedral model, whereas for the Na–He$_{24}$ cluster, spherical symmetry is assumed (Fig. 1). For each cluster we have chosen a set of Na–He radial distance and with the specific number of atoms in the cluster which can be fitted for the geometry of the cluster. For each radial distance between Na and He atoms, and the specified geometry Hartree-Fock (HF), calculations have been performed to generate the reference orbitals for subsequent SAC-CI calculations using Gaussian 03 program [22]. In all cases the basis set for Na is contracted 6s5p3d1f with diffuse s + p type functions based on Mclean and Chandler [23], whereas the basis set for He is 5s + 1s and is based on double zeta of Dunning and Hay [24] with diffuse s type functions; the exponents being obtained from the extrapolation of the outer orbitals. Full active space calculation was performed for all cases. Therefore active spaces used are 119, 167 and 191 for Na–He$_{12}$, Na–He$_{20}$ and Na–He$_{24}$, respectively. Initially for the isolated Na atom, the HF and SAC-CI single and double excitation operators (*SD-R*) calculation was performed to find the lowest allowed excitation state. To reduce the computational effort, the perturbation selection scheme was adopted [18]. The threshold of the linked terms for the ground state was set to $\lambda_g = 1.0 \times 10^{-6}$ au. The unlinked terms were described as the product of the linked operators with SDCI coefficients larger than 0.005. For

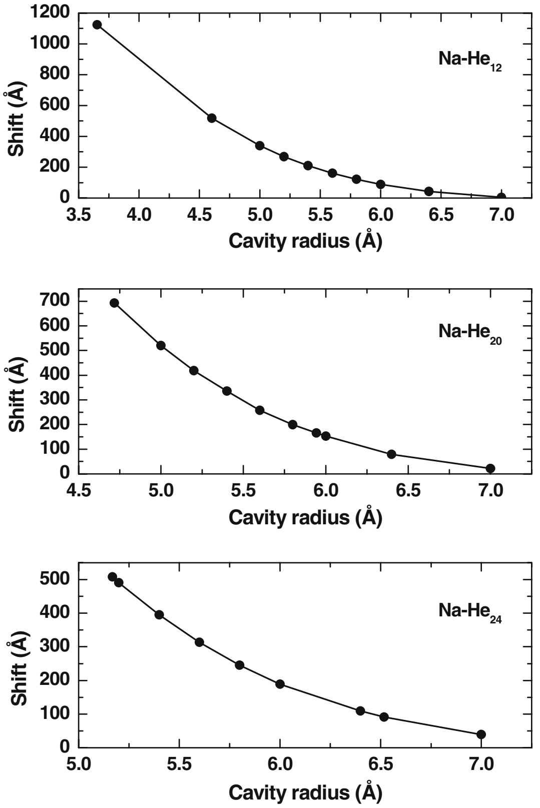


Fig. 3 Plot of wavelength shift of the $^2P \leftarrow {}^2S$ principal resonance line against cavity radius for different Na–He$_n$ clusters

excited states, the threshold of the linked doubles was set to $\lambda_e = 1.0 \times 10^{-7}$ au. The thresholds of the CI coefficients for calculating the unlinked operators were 0.05 and 0.00 for the R and S operators, respectively.

3 Results and discussion

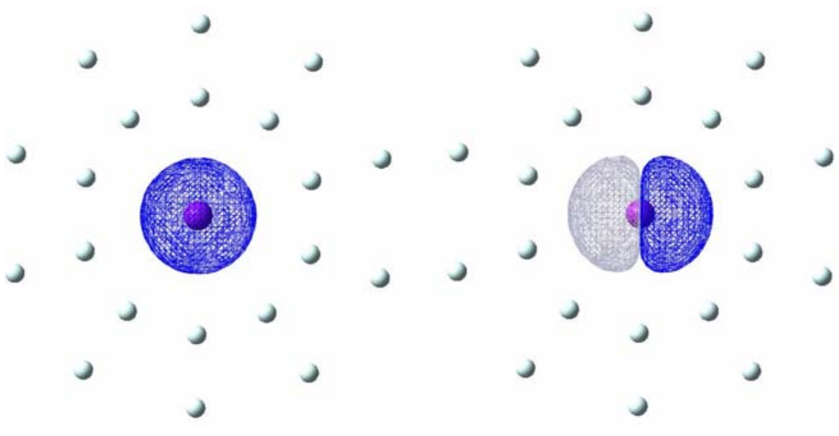
The wavelength corresponding to 3p ←3s transition comes out to be 5968 Å with an error of ∼1.3% from the experimental wavelength ∼5893 Å, and this will act as the reference level from which the shift because of He cluster will be evaluated. To note the consistency of the basis sets, we estimated the basis set superposition errors (BSSE), and a plot is given in Fig. 2 for various cavity radii used for our cluster calculations. The errors are indeed small indicating the consistency of our basis sets. The changes in wavelength of the Na 'D' line in presence of surrounding He cluster are displayed in Table 1. The oscillator strengths (f_{LHe}) connected with the transition has also been shown in Table 1. It is noted that with increase of the Na–He distance the shift diminishes. This is physically obvious as with increase of this distance the Na–He interaction diminishes and also the influence because of He–He distance.

Figure 3 shows the plot of the wavelength shift $\Delta\lambda$ against bubble radius r. The nature of the change is physically meaningful as the shift depends mainly on the strength of the Na–He pair potential which diminishes more rapidly than is compensated by the increase of the number of surrounding He-atoms because of enhanced bubble radius. We have also evaluated $\Delta\lambda$ for two special radial distances, namely the distance at which the liquid helium goes to its bulk density ρ_0 (0.0218 Å^{-3}) and at the distance where the density become $\rho_0/2$. The latter distance has been defined as the effective bubble radius in literature [7,12]. We fix the number of nearest neighbors according to our choice of the clusters. With the choice of a fixed density (either ρ_0 or $\rho_0/2$) of surrounding He atoms the bubble radius has been calculated using the formula given by Gspann [11]

$$N_{\text{neigh}} = \left(4^{4/3}\pi/\sqrt{3}\right)\left(r\rho^{1/3}\right)^2$$

where N_{neigh} is the coordination number, that is the number of helium atoms finding a place on the sphere of radius r, ρ is the respective number density of the helium liquid, viz. 0.0218 Å^{-3} for ^{4}He. With this bubble radius the entire cal-

Fig. 4 The s- and p-orbitals of Na atom embedded in Na–He$_{20}$ helium cluster. Iso value = 0.001. Na—*violet* (dark), He—*pale blue* (light)



s-orbital ($r = 5.9434$ Å) p-orbital ($r = 5.9434$ Å) culations are repeated to get the shift. The results for such calculations have also been displayed in Table 1. From an analysis of the results shown in Table 1 we notice that for a cluster of 20 He atoms surrounding central Na, the shift $\Delta\lambda$ for the realistic liquid He density $\rho_0/2$ ($\sim$0.0109 Å^{-3}) corresponding to the effective bubble radius 5.9434 Å comes out to be $\sim$166 Å with the oscillator strength (f_{LHe}) value of 0.3311. The estimated existing theoretical results vary from $\sim$150 to 167 Å [7,12]. The p-type orbitals are degenerate in the free Na atom. From our excitation calculations we find that this degeneracy is not lifted when the Na atom is embedded in the liquid helium. Hence, we get three 3p ← 3s degenerate states for every Na–He$_n$ cluster. The nature of the ground and excited states profile for the Na atom are shown in Fig. 4 for Na–He$_{20}$ cluster with a cavity radius of 5.9434 Å. It appears that the profiles are not distorted during excitation. The situation would be expected to be appreciably different after relaxation of the bubble. These s- and p-orbitals of Na embedded in liquid helium environment have been drawn using GaussView 03 program package [25].

4 Conclusions

The excitation line shift of the principal ^{2}P ← ^{2}S resonance line of sodium atom embedded in liquid helium has been estimated using SAC-CI method considering to various Na–He$_n$ model clusters. The shift of transition energy depends on both the cluster size as well as on the bubble radius. For the Na–He$_{20}$ cluster with a bubble radius of 5.9434 Å the shift 166 Å is in conformity with those reported earlier and is very encouraging from the point of view of cluster calculations.

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