

Ab initio study of NaRb^+ : Potential energy curves, spectroscopic constants and atomic polarizabilities

C. Ghanmi ^a, H. Bouzouita ^a, N. Mabrouk ^a, H. Berriche ^{a,b,*}

^a *Laboratoire de Physique et Chimie d'Interfaces, Département de Physique, Faculté des Sciences de Monastir, Avenue de l'Environnement, 5019 Monastir, Tunisia*

^b *Physics Department, Faculty of Sciences, King Khalid University, PO Box 9004, Abha, Saudi Arabia*

Received 21 June 2006; received in revised form 16 December 2006; accepted 19 December 2006

Available online 27 December 2006

Abstract

Using an ab initio approach involving a non-empirical pseudopotentials for Na and Rb atoms, the adiabatic potential energy curves of 26 electronic states of NaRb^+ ionic molecule dissociating up to $\text{Na}(4p) + \text{Rb}^+$ and $\text{Na}^+ + \text{Rb}(7s)$ have been investigated. Their molecular spectroscopic constants have been derived and compared with the available theoretical works. Furthermore, the transition dipole moments from $X^2\Sigma^+$ and $2^2\Sigma^+$ to higher excited states have been determined. Numerous avoided crossings between electronic states of $^2\Sigma^+$ and $^2\Pi$ symmetries have been localised and analysed. Their existences are related to the charge transfer process between the two ionic systems Na^+Rb and NaRb^+ . The accurate potential energy curves have been exploited to realize a long-range vibrational level spacing analysis using the WKB semi-classical approximation in order to extract the Na and Rb atomic static dipole polarizabilities. A very good agreement between our static dipole polarizabilities and the available experimental and theoretical works has been observed. © 2007 Elsevier B.V. All rights reserved.

Keywords: Ab initio; Pseudopotentials; NaRb^+ ; Spectroscopic constants; WKB approximation; Polarizability; Alkali atoms

1. Introduction

The theoretical investigation of the XY^+ ($X, Y = \text{Li, Na, K, Rb}$ and Cs) ionic molecules is of great importance for understanding the nature of intermolecular interactions and radiative transition. However, the potential energy curves and the transition dipole moment constitute a basic data to study dissociation process. In particular, the XY^+ alkali ionic systems present an interesting long range behaviour dominated by charge dipole interactions. In fact, the intermolecular potential and the interactions at long range play an important role in the calculation of the properties of the atoms as well as their electric (hyper) polarizability. These properties present an interesting role in the

evaluation of the core–core interaction. In addition, the electric (hyper) polarizabilities are important to evaluate the weak coulombic interaction between an alkali atom and an alkali cation at long range, which governs the potential energy curves of ionic molecules at large interaction distances [1–3].

In this study, the NaRb^+ ionic system was treated using an ab initio calculation based on pseudopotentials technique [4]. This technique has reduced the number of active electrons of NaRb^+ molecule to only one electron. The electronic energy was calculated at the SCF level and it was corrected by taking into account the core–core and core–valence electron correlation following the formalism of Foucrault et al. [5]. The non-empirical pseudopotentials permit the use of very large basis sets for the valence and Rydberg states and allow accurate description for the highest excited states. We have recently published ab initio studies of a large number of states for a large range of

* Corresponding author. Tel.: +216 22768161; fax: +216 73500278.

E-mail addresses: hamid.berriche@fsm.rnu.tn, hberriche@kku.edu.sa (H. Berriche).

internuclear distances for LiNa⁺ [6], LiK⁺ [7], NaK⁺ [8,9] and KRb⁺ [3]. We extend here these previous works to NaRb⁺ ionic molecule.

In this paper, we report the results of an ab initio calculation for 26 electronic states of ²Σ⁺, ²Π and ²Δ symmetries of the NaRb⁺ ionic molecule up to the dissociation limits Na(4p) + Rb⁺ and Na⁺ + Rb(7s). In Section 2 we present briefly the methods used to compute the electronic energy and to realize the vibrational spacing analysis near the dissociation limit. Section 3 is devoted to present our results: spectroscopic constants, transition dipole moments and Na and Rb atomic polarizabilities. Finally we conclude.

2. Summary of calculations

The computational method is the same as that used in our previous works on LiNa⁺, LiK⁺, NaK⁺ and KRb⁺ ionic molecules [3,6–9]. The use of the pseudopotentials technique [4] for NaRb⁺ cores has reduced the number of active electrons to only one electron, where the SCF calculation has produced the exact energy within the basis set limitation. Furthermore, the SCF energy is corrected by taking into account the core–core and core–valence electron correlation following the formalism of Foucrault et al. [5]. The non-empirical pseudopotentials permit the use of very large basis sets for the valence and Rydberg states and allow accurate description for the highest excited states. The Na and Rb atoms are treated through the one-electron pseudopotentials proposed by Barthelat and Durand [4]. For sodium, we used the Gaussian basis set (7s, 6p, 5d, 3f/6s, 5p, 4d, 2f) of [6], while for rubidium we used the Gaussian basis set (7s, 4p, 5d, 1f/6s, 4p, 4d, 1f) of [10]. The cut-off radii, reported in Table 1, were optimised to reproduce the ionisation potentials and the lowest s, p, d and f one electron states as deduced from the atomic data table. The core dipole polarizability of the ionic atoms Na⁺ and Rb⁺, have been taken to the experimental ones, respectively, 0.993 a₀³ and 9.245 a₀³. In this calculation, we have used 22.9897 and 85.4678 uma as atomic masses for, respectively, Na and Rb atoms.

For the vibrational spacing analysis, we have used the WKB semi-classical method. An excellent review of the semi-classical approximation applied to the vibrational diatomic molecules can be found in [11]. Here, we present briefly the used formalism to perform a long range potential analysis. The WKB semi-classical approximation applied to a potential of the following expression:

$$V(R) = D - \frac{C_n}{R^n} \quad (1)$$

Table 1
l-dependant cut-off radii (in bohr) for Na and Rb atoms

l	Na	Rb
s	1.4423	2.5213
p	1.625	2.279
d	1.5	2.511
f	1.5	2.511

where D is the asymptotic limit, leads to an analytical expression for the vibrational energy levels

$$E(v) = D - \left((v_D - v) \frac{n-2}{2n} K_n \right)^{\frac{2n}{n-2}} \quad (2)$$

v_D is the real (non-integer) number corresponding to the last vibrational level near the dissociation energy limit and K_n is given by

$$K_n = \hbar \sqrt{\frac{2\pi \Gamma(1 + \frac{1}{n})}{\mu \Gamma(\frac{1}{2} + \frac{1}{n})}} \frac{n}{(C_n)^{\frac{1}{n}}} \quad (3)$$

In our case, at long range distance, the potential energy behaves as a charge–dipole interaction and $n = 4$. Using the last expression for the vibrational energy levels, the $(E_v - D)^{(1/4)}$ can be written as following:

$$(E_v - D)^{\frac{1}{4}} = -(v_D - v) \frac{K_4}{4} \quad (4)$$

The plot of $(E_v - D)^{(1/4)}$ versus v should be purely linear. A least square fit of this linear law allows us to determine rather accurately the v_D and C_4 constants from which all vibrational levels near the dissociation limit and also the related classical turning points ($R_c(v)$) can be easily determined according to

$$E(v) = D - 11.817045(v_D - v)C_4^{-1}\mu^{-2} \quad (5)$$

$$R_c(v) = C_4^{\frac{1}{4}}(D - E(v))^{-\frac{1}{4}} \quad (6)$$

3. Results and discussion

3.1. Potential energy curves and spectroscopic constants

The potential energy curves for all the electronic states of NaRb⁺ dissociating into Na(3s, 3p, 4s, 3d, 4p, 5s, 4d) + Rb⁺ and Na⁺ + Rb(5s, 5p, 4d, 6s, 6p, 5d, 7s) have been computed for a large and dense grid of intermolecular distances from 4 to 300 a.u. Such potential energy curves are displayed in Fig. 1 for ²Σ⁺ (solid line), ²Π (dashed line) and ²Δ (dotted line) states. We remark that the ground state has the deepest well ($D_e = 3718 \text{ cm}^{-1}$) compared to the ²Σ⁺ excited states or other symmetries, which shows the electron delocalisation and the formation of a real chemical bond. The spectroscopic constants (R_e , D_e , ω_e and B_e) of the ground and low lying states are presented in Tables 2 and 3 and compared with the main available theoretical works realised by Valance et al. [12,13] and Romero et al. [14]. For our best knowledge, there is no experimental work on such system. Valance et al. [12,13] have reported in their work the potential energy curves and their spectroscopic constants of the ground and the first six excited states of the NaRb⁺ ionic molecule. Their adiabatic energy has been calculated for a small grid of intermolecular distances; from 4 to 20 a.u. Romero et al. have performed a diabatic diagram from an analysis of the adiabatic electronic wave functions. They have used

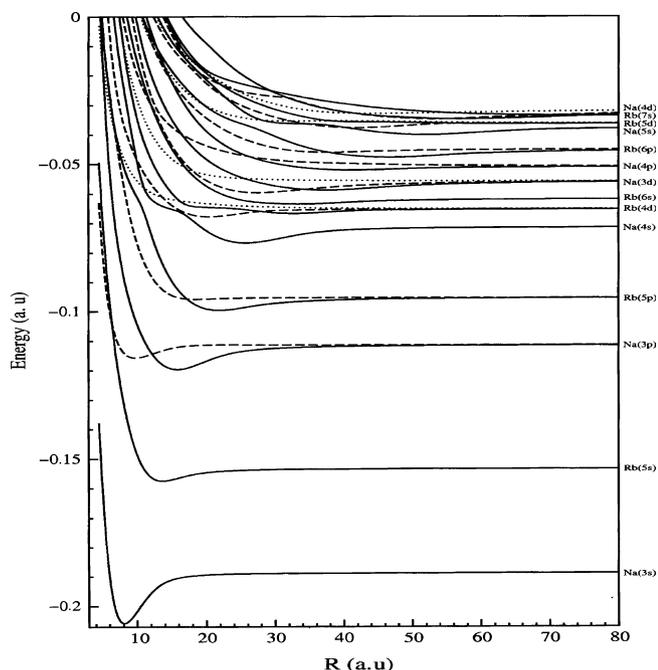


Fig. 1. Potential energy curves for the $2\Sigma^+$ (solid line), the 2Π (dashed line) and the 2Δ (dotted line) electronic states of NaRb^+ ionic molecule dissociating into $\text{Na}(3s, 3p, 4s, 4p, 5s, 5p, 6s, 6p, 7s) + \text{Rb}^+$ and $\text{Rb}(3s, 3p, 4s, 4p, 5s, 5p, 6s, 6p, 7s) + \text{Na}^+$.

in their study the same formalism used in this work. They have presented the spectroscopic constants of only $1-4^2\Sigma^+$ and $1^2\Pi$ states for a range of internuclear distances between 4 and 40 a.u. In our study, the potential energy has been carried out for a dense and large grid of internuclear distances, from 4 to 300 a.u. Thus has allowed us to

evaluate the equilibrium distances and the potential wells located at intermediate and large distances. Table 2 corresponds to a comparison between our spectroscopic constants of the ground and the first six excited states and those of other theoretical works [12–16]. Our ground state equilibrium distance (R_e) is in good agreement as well as the well depth (D_e) with the work of Valance et al. [12]. We find for the R_e and D_e , respectively, 8.10 a.u. and 3718 cm^{-1} and they found 7.50 a.u. and 3847 cm^{-1} . For the $2^2\Sigma^+$ they reported the spectroscopic constants $R_e = 14.00\text{ a.u.}$ and $D_e = 1371\text{ cm}^{-1}$ to be compared with our values of, respectively, 13.66 a.u. and 887 cm^{-1} . If a rather good agreement is observed for the equilibrium distance, their potential is much deeper. For the $3^2\Sigma^+$ and $1^2\Pi$ states, Valance et al. [12] have reported in their paper that these states exhibit small potential wells equal, respectively, to 607 and 155 cm^{-1} . In contrast, in our work both states present important well depths of, respectively, 1777 and 908 cm^{-1} . The $4, 5^2\Sigma^+$ and $2^2\Pi$ electronic states are in our work attractive and they have potential wells of, respectively, $904, 1134$ and 86 cm^{-1} located at, respectively, $21.89, 25.81$ and 18.69 a.u. This is in disagreement with the study of Valance et al. [12] as such states have been found to be repulsive. It is important to note that Valance et al. [12] have calculated their potential energy curves to a maximum distance limit of 20 a.u. , which is smaller than the equilibrium distances of the $4^2\Sigma^+$ and $5^2\Sigma^+$ states. From the comparison between our work and that of Valance et al. [12], we remark once, a good agreement between the two works for $1, 2, 3^2\Sigma^+$ and $1^2\Pi$ states. A disagreement is observed for the $4, 5^2\Sigma^+$ and $2^2\Pi$ states. In our work, all these states are attractive in contrast to the work

Table 2
Spectroscopic constants of the ground and the first six $2^2\Sigma^+$ and $2^2\Pi$ electronic states of NaRb^+

State	R_e (a.u.)	D_e (cm^{-1})	T_e (cm^{-1})	ω_e (cm^{-1})	B_e (cm^{-1})	Ref.
$1^2\Sigma^+$	8.10	3718		76.04	0.050635	This work
	7.50	3847				[12]
	8.10	3716		77.33		[14]
	7.90	3968				[15]
	7.90	4436				[16]
$2^2\Sigma^+$	13.66	887	10,582	32.80	0.017822	This work
	14.00	1371				[12]
	13.65	891		38.19		[14]
$3^2\Sigma^+$	15.87	1777	18,910	29.21	0.013192	This work
	16.00	607				[12]
	15.85	1775		33.94		[14]
$1^2\Pi$	9.77	908	19,779	33.63	0.034796	This work
	12.00	155				[12]
	9.78	910		36.23		[14]
$4^2\Sigma^+$	21.89	904	23,312	17.53	0.006938	This work
Repulsive						[12]
$2^2\Pi$	18.69	86	24,130	12.61	0.009527	This work
	Repulsive					[12]
$5^2\Sigma^+$	25.81	1134	28,346	16.22	0.004991	This work
Repulsive						[12]

Table 3
Spectroscopic constants of the higher excited ${}^2\Sigma^+$, ${}^2\Pi$ and ${}^2\Delta$ electronic states of NaRb^+

State	R_e (a.u.)	D_e (cm^{-1})	T_e (cm^{-1})	ω_e (cm^{-1})	B_e (cm^{-1})
$6^2\Sigma^+$	32.75	309	30,524	9.40	0.003099
$3^2\Pi$	20.47	549	30,286	16.52	0.007933
$1^2\Delta$	Repulsive				
$7^2\Sigma^+$	33.31	356	31,224	6.90	0.002990
$8^2\Sigma^+$	37.64	635	32,259	6.91	0.002359
$4^2\Pi$	27.55	825	32,069	11.53	0.004378
$2^2\Delta$	Repulsive				
$9^2\Sigma^+$	41.36	248	33,745	6.69	0.001945
$5^2\Pi$	Repulsive				
$10^2\Sigma^+$	46.64	589	34,689	7.36	0.001528
$6^2\Pi$	38.08	214	35,064	5.73	0.002298
$11^2\Sigma^+$	52.02	554	36,378	6.90	0.001228
$12^2\Sigma^+$	Repulsive				
$7^2\Pi$	42.08	287	36,901	6.85	0.001885
$3^2\Delta$	Repulsive				
$13^2\Sigma^+$	57.80	216	37,564	4.39	0.000995
$14^2\Sigma^+$	72.49	457	37,864	4.52	0.000632
$8^2\Pi$	53.36	719	37,564	6.45	0.001167
$4^2\Delta$	44.25	294	37,963	3.40	0.001713

of Valance et al. [12] where all such electronic states are repulsive.

The comparison between our spectroscopic constants and those of Romero et al. [14] presents a very good agreement for all $1-3^2\Sigma^+$ and $1^2\Pi$ electronic states. The differences between our and their spectroscopic constants does not exceed 0.02 a.u. for R_e and 4 cm^{-1} for D_e . Such excellent agreement between our results and those of Romero et al. is not surprising as we used the same method and it is expected to obtain similar agreement for the higher excited states. For our best knowledge, the spectroscopic constants for ${}^2\Sigma^+$, ${}^2\Pi$ and ${}^2\Delta$ higher excited states are presented here for the first time (see Table 3). The equilibrium distance of all these states is found at intermediate and large values of internuclear distances. All of the $6-11$, 13 and $14^2\Sigma^+$ excited states are attractive with potential well depths of some 100 cm^{-1} . We note that the $12^2\Sigma^+$ electronic state dissociated into $\text{Rb}(5d) + \text{Na}^+$ is repulsive. The higher $3, 4, 6-8^2\Pi$ excited states, except the $5^2\Pi$ which is repulsive, are attractive with small potential wells of some 100 cm^{-1} of depths. The $1-3^2\Delta$ are found in our work to be repulsive, however the $4^2\Delta$ is attractive. It has a well depth of 294 cm^{-1} located at an equilibrium distance of 44.25 a.u.

We remark in the potential energy curves many avoided crossings between electronic states of same symmetries for ${}^2\Sigma^+$ and ${}^2\Pi$ states. The existence of such avoided crossings is related to the charge transfer process between the two ionic systems Na^+Rb and NaRb^+ . In Table 4 we present the internuclear distance R_c , which corresponds to the avoided crossings between $4/5, 5/6, 6/7, 8/9, 9/10, 10/11, 11/12, 12/13$ and $13/14\ {}^2\Sigma^+$, and $4/5, 5/6$ and $7/8\ {}^2\Pi$ states dissociating into both systems $\text{Na} + \text{Rb}^+$ and $\text{Na}^+ + \text{Rb}$. Most of the avoided crossings are due to the charge transfer between each two states and finally between Na and Rb atoms. Many theoretical works on measuring cross section of the electron transfer between Li and Na in the LiNa^+

Table 4
 R_c (in a.u.): the avoided crossing distance positions

State	R_c position
$4^2\Sigma^+/5^2\Sigma^+$	10.990
$5^2\Sigma^+/6^2\Sigma^+$	16.685
$6^2\Sigma^+/7^2\Sigma^+$	7.185
$8^2\Sigma^+/9^2\Sigma^+$	8.500
$9^2\Sigma^+/10^2\Sigma^+$	7.000
	13.000
$10^2\Sigma^+/11^2\Sigma^+$	27.485
$11^2\Sigma^+/12^2\Sigma^+$	17.765
	37.745
$12^2\Sigma^+/13^2\Sigma^+$	14.255
	19.380
$13^2\Sigma^+/14^2\Sigma^+$	7.905
	29.250
	80.005
$4^2\Pi/5^2\Pi$	12.665
$5^2\Pi/6^2\Pi$	6.720
$7^2\Pi/8^2\Pi$	18.245
	55.990

[6,17–20] and Li and K in the LiK^+ [7] ionic molecules were realised in the past. Another work [21] using the avoided crossing between the $4^2\Sigma^+$ and $5^2\Sigma^+$ states of the LiNa^+ molecule was done recently to study the non-adiabatic dynamics by two-colour ATD experiment. For our best knowledge, there are no similar works on the NaRb^+ molecule. For this aim, we have determined with accuracy the position of such avoided crossings for further use. Some curves present more than two positions of avoided crossing leading to an undulating feature of the potential of some excited states.

3.2. Transition dipole moment

In addition to the potential energy curves and the spectroscopic constants, we report in this work on NaRb^+ ionic

molecule, the adiabatic transition dipole moment from $X^2\Sigma^+$ and $2^2\Sigma^+$ states dissociating, respectively, into $\text{Na}(3s) + \text{Rb}^+$ and $\text{Na}^+ + \text{Rb}(5s)$ to higher excited states. Fig. 2 corresponds to transition dipole moment from $X^2\Sigma^+$ to other excited states. We remark that the most important one present the transition moment between $X^2\Sigma^+$ and $2^2\Sigma^+$ states which has a maximum of 3.313 a.u. located at 11.10 a.u. At this distance the two states present also a maximum overlap between their molecular orbital. It is expected that the photo absorption spectrum will present a peak around this distance. At infinite distance, the transition dipole moment vanishes as the electron in the ground state is on the Na atom and in the first excited state on Rb atom corresponding to an electron transfer between two different species $\text{Na}(3s)$ and $\text{Rb}(5s)$. The $X^2\Sigma^+ \rightarrow 3^2\Sigma^+$ transition dipole moment starts from small values then increases rapidly between 10 and 20 a.u. and finally becomes constant equal to 2.422 a.u., corresponding to the atomic transition dipole moment between $\text{Na}(3s)$ and $\text{Na}(3p)$ to be compared with the experimental value of 2.377 a.u. The transitions from $X^2\Sigma^+$ to higher excited states are less important. They go to zero when the atomic transition is forbidden (from Na to Rb) and to a constant when the transition is allowed and corresponding at very large distance to the pure atomic transition. We have also drawn on Fig. 3 the transition dipole moment between the first excited state $2^2\Sigma^+$ dissociating into $\text{Na}^+ + \text{Rb}(5s)$ and the higher excited states. We obtain the same behaviour as we have got in Fig. 2 for transition dipole moment between the $X^2\Sigma^+$ state and the higher

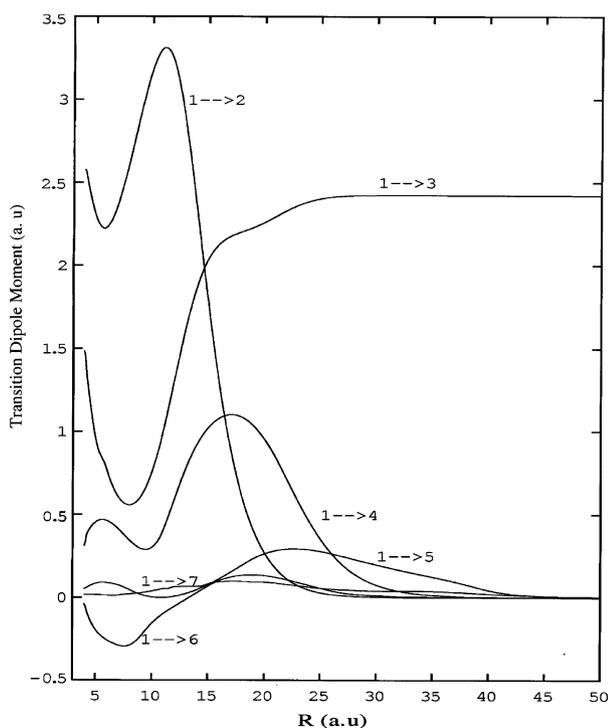


Fig. 2. Transition dipole moment from $X^2\Sigma^+$ to the higher $2^2\Sigma^+$ excited states.

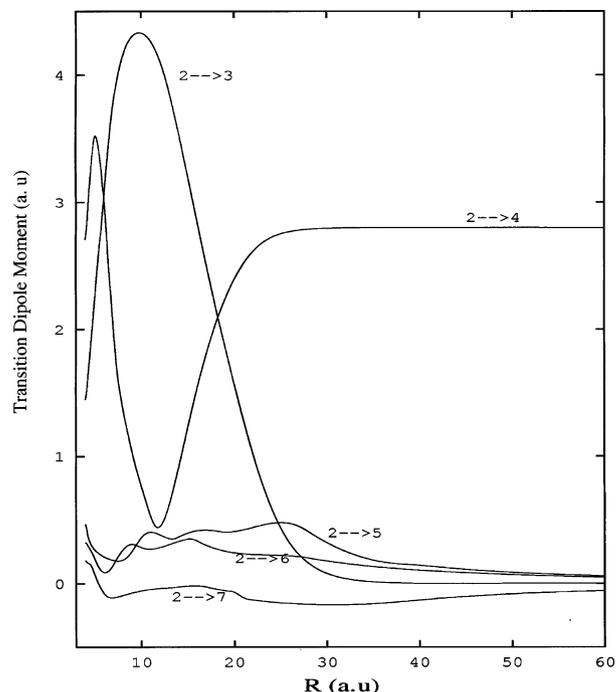


Fig. 3. Transition dipole moment from $2^2\Sigma^+$ to the higher $2^2\Sigma^+$ excited states.

excited states. The most important transition is from $2^2\Sigma^+$ to $3^2\Sigma^+$ states dissociating into two different molecular systems $\text{Na}^+ + \text{Rb}(5s)$ and $\text{Na}(3p) + \text{Rb}^+$. It has a maximum equal to 4.332 a.u. around 9.64 a.u. then it decreases rapidly to zero. At large distance, the transition from $2^2\Sigma^+$ to $4^2\Sigma^+$ states, which is related to the atomic transition $\text{Rb}(5s) \rightarrow \text{Rb}(5p)$, is constant (2.797 a.u.). We remark from Fig. 3 that the transitions from $2^2\Sigma^+$ to 5, 6, 7 and $8^2\Sigma^+$ states are small and vanish or become constant depending on the nature of the atomic transition.

3.3. Atomic polarizabilities

Many papers concerning the experimental [25–29] and the theoretical [22–24,30] evaluation of the static dipole polarizabilities of the alkali atoms were reported in the literature. In this section, the aim is to show that the high accuracy of the potential energy curves can be exploited to perform a computing of the atomic polarizabilities using a simple calculation based on the WKB semi-classical approximation and a vibrational spacing analysis near the dissociation limit. Furthermore, such accuracy will be tested through the comparison of our calculated static polarizabilities with the available experimental and theoretical references. The WKB semi-classical approximation, will give us additional information on the long range potential interactions through the preliminary vibrational level progression and based on the remarkable adequacy of the linear fit of $(E_v - D)^{(1/4)}$. According to the relation (4), a plot of $(E_v - D)^{(1/4)}$ versus v for several $N^2\Sigma^+$ ($N = 1-5, 7, 9-11$) electronic states is purely linear (see

Fig. 4). These plots are remarkably linear except for the last points of some curves. In fact, the deviation from the linear law for the last points can be taken as a measure of the numerical limitations of the Numerov propagation method near the dissociation limit. This assumption is particularly clear for $1^2\Sigma^+$ and $2^2\Sigma^+$ states. Furthermore, using this fit we can find the total number of vibrational levels trapped by each state (see Table 5) and especially the last excited vibrational levels near the dissociation limit.

The calculation of the atomic polarizabilities has been performed for various ns and np states of Na and Rb atoms. Our values are reported in Table 5 and compared with the other experimental [25–29] and theoretical [22–24,30] ones. Magnier et al. [22], in a recent work, have realized a systematic evaluation of the ground and various states for alkali atoms. Their calculation has been performed using model potential atomic functions expanded in terms of rather large Slater-type orbital sets. Our polarizabilities of the ground states of Na and Rb atoms are, respectively, 151.6 and 311.1 a.u. to be compared with the experimental [25] values of, respectively, 159 ± 3 and 319 ± 6 a.u. The difference between the various experimental works is about 5 a.u. for Na and 10 a.u. for Rb. Magnier et al. have reported the polarizabilities of, respectively, 165 and 335 a.u. for Na and Rb ground states. For the 2S excited states, we present the polarizabilities of Na(4s) and Rb(6s) atomic states which are, respectively, 3069.8 and 5253.4 a.u. They are in very good agreement with Magnier et al. [22] values. The differences between our polarizabilities and those of Magnier et al. [22] are, respectively, 25.2 a.u. for Na(4s) and 16.6 a.u. for Rb(6s). We present also in Table 5 the polarizabilities of the 2P

Table 5

The static dipole polarizabilities of various atomic ns 2S and np_m ($m = 1$) 2P levels

Na	v_D	Rb	v_D	Ref.		
3s	151.6	119.6	5s	311.1	89.3	This work
	165			335		[23]
	162			320		[24]
	162.88 ± 0.6					[25]
	159 ± 3			319 ± 6		[26]
	164.7 ± 11.5			329 ± 23		[27]
	162.7 ± 0.8					[28]
	159.4 ± 13.5					[29]
	162.6 ± 0.3					[30]
4s	3069.8	166	6s	5253.4	148	This work
	3095			5270		[23]
	3086					[23]
3p ₀	292.6	197.6	5p ₀	859	192.2	This work
	273			700		[23]
3p _{±1}	395.8		5p _{±1}	881.6		This work
	403			923		[23]
4p ₀	−4638.5	171.9	6p ₀	11083.9	292.9	This work
	−4646			10,913		[23]
4p _{±1}	−4496.1		6p _{±1}	13316.5		This work
	−4437			13,579		[23]

excited states. They are in very good agreement with those of Magnier et al. [22]. For our best knowledge there is no experimental study on these states.

4. Conclusion

The adiabatic potential energy curves of 26 electronic states and their spectroscopic constants of NaRb⁺ ionic molecule dissociating up to Na(4p) + Rb⁺ and Na⁺ + Rb(7s) have been calculated using ab initio approach based on the pseudopotentials techniques. In addition, a core–core and core–valence correlations have been taken into account. A good agreement between our spectroscopic constants and those of the theoretical work of Valance et al. [12] is observed. In particular an excellent agreement is observed with the theoretical study of Romero et al. [14]. Unfortunately, they reported only the spectroscopic constants of $1-3^2\Sigma^+$ and $1^2\Pi$ states. The spectroscopic properties of the higher excited states are reported here for the first time. In addition, we have determined the transition dipole moment from $X^2\Sigma^+$ and $2^2\Sigma^+$ states to higher excited states. The accurate determined potential energy curves are exploited to perform a long-range vibrational spacing analysis using the WKB approximation in order to extract the static dipole polarizabilities of Na and Rb atoms. A general agreement is observed between our evaluated polarizabilities and other theoretical and experimental works. Thus shows again the high accuracy of our ab initio calculation. Finally the produced data such as the potential energy curves, the transition dipole moments and the atomic polarizabilities constitute an important support for both theoretical and experimental further use.

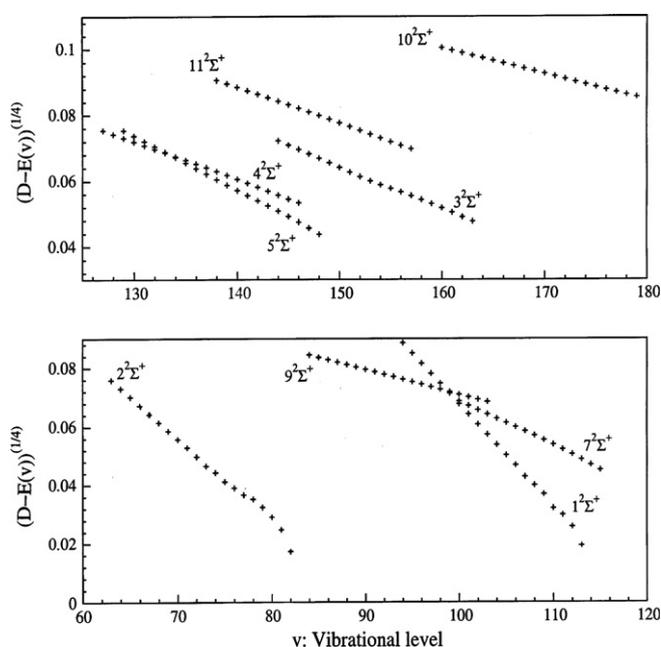


Fig. 4. Plot of $(E_v - D)^{1/4}$ versus v for 1–5, 7, 9–11 $^2\Sigma^+$ electronic states.

References

- [1] C. Ghanmi, H. Berriche, H. Ben Ouada, Lect. Ser. Comput. Comput. Sci. 1 (2004) 1061.
- [2] C. Ghanmi, H. Berriche, H. Ben Ouada, Comput. Mater. Sci. 38 (2007) 494.
- [3] C. Ghanmi, H. Berriche, H. Ben Ouada, Lect. Ser. Comput. Comput. Sci. 4 (2005) 703.
- [4] J.C. Barthelat, Ph. Durand, Gazz. Chim. Ital. 108 (1978) 225; Ph. Durand, J.C. Barthelat, Theor. Chim. Acta 38 (1975) 283.
- [5] M. Foucrault, Ph. Millié, J.P. Daudey, J. Chem. Phys. 96 (1992) 1257.
- [6] H. Berriche, J. Mol. Struct. (Theochem) 663 (2003) 101.
- [7] H. Berriche, C. Ghanmi, H. Ben Ouada, J. Mol. Spectrosc. 230 (2005) 161.
- [8] C. Ghanmi, H. Berriche, H. Ben Ouada, J. Mol. Spectrosc. 235 (2006) 158.
- [9] C. Ghanmi, H. Berriche, H. Ben Ouada, in: Proceeding of the International Conference on Computational and Mathematical Methods, in Science and Engineering, CMMSE-2005, Alicante, June 27–30, 2005, 166.
- [10] D. Pavolini, T. Gustavsson, F. Spiegelmann, J.-P. Daudey, J. Phys. B: Atom. Mol. Opt. Phys. 22 (1989) 1721.
- [11] J. Vigué, Ann. Phys. (Paris) 3 (1982) 155.
- [12] A. Valance, A. Bernier, M. Elmaddarsi, Chem. Phys. 103 (1986) 151.
- [13] A. Valance, J. Chem. Phys. 69 (1978) 355.
- [14] T. Romero, J. de Andrés, M. Albertí, J.M. Lucas, J. Rubio, J.P. Daudey, A. Aguilar, Chem. Phys. Lett. 261 (1996) 583.
- [15] L. von Szentpaly, P. Fuentealba, H. Preuss, H. Stoll, Chem. Phys. Lett. 93 (1982) 555.
- [16] W. Schwartzmann, Ph.D. Thesis, Bochum, FRG, 1979.
- [17] H.L. Dadey, J. Perel, in: Proceeding of the Sixth International Conference on the Physics of Electronic and Atomic Collisions, North-Holland, Amsterdam, 1969. Abstract, p. 600.
- [18] V. Aquilanti, G.P. Bellu, J. Chem. Phys. 61 (1974) 1618.
- [19] M. Machholm, C. Courbin, J. Phys. B 29 (1996) 1079.
- [20] J.W. Thomson, J. Salgado, N. Andersen, D. Dowek, A. Dubuois, J.C. Houver, S.E. Nielsen, A. Svenssen, J. Phys. B 32 (1999) 5189.
- [21] S. Magnier, A. Toniolo, Chem. Phys. Lett. 338 (2001) 329.
- [22] S. Magnier, M. Aubert-Frécon, J. Quant. Spectrosc. Rad. Transfer. 75 (2002) 121.
- [23] P. Fuentealba, O. Reyes, J. Phys. B: Atom. Mol. Opt. Phys. 26 (1993) 2245.
- [24] A.J. Thakkar, C. Lupinetti, Chem. Phys. Lett. 402 (2005) 270.
- [25] R.W. Molof, H.L. Schwartz, Th.M. Miller, B. Bederson, Phys. Rev. A 10 (1974) 1131.
- [26] W.D. Hall, J.C. Zorn, Phys. Rev. A 10 (1974) 1141.
- [27] C.R. Ekstrom, J. Schmiedmayer, M.S. Chapman, T.D. Hammond, D.E. Pritchard, Phys. Rev. A 51 (1995) 3883.
- [28] D. Rayane, A.R. Allouche, E. Benichou, R. Antoine, M. Aubert-Frécon, Ph. Dugourd, M. Broyer, C. Ristori, F. Chandezon, B.A. Huber, C. Guet, Eur. Phys. J. D 9 (1999) 243.
- [29] A. Derevianko, W.R. Johnson, M.S. Safronova, J.F. Babb, Phys. Rev. Lett. 82 (1999) 3589.
- [30] Th.M. Miller, B. Bederson, Adv. Atom. Mol. Phys. 25 (1988) 1.