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Theoretical study of the low-lying adiabatic states of the $NaLi^+$ molecular ion

Djamal Rabli, Ronald McCarroll

Sorbonne Université, Université Pierre et Marie Curie, UMR 7614 du CNRS,
Laboratoire de Chimie Physique-Matiére et Rayonnement, 75231-Paris Cedex 05, France

Abstract

With one active electron, the $NaLi^+$ cation is a relatively simple system to study, and a good candidate for which results issue from different approaches can be compared to cross check the reliability of different theoretical methods for the calculation of the adiabatic potential energies. However, comparison of the *ab-initio* results of Berriche (2003) and those of Magnier and Frécon (2001), employing model potential methods, is showing a serious disagreement concerning several molecular states. In particular, the low-lying states $2^2\Sigma^+, 4^2\Sigma^+, 6^2\Sigma^+, 8^2\Sigma^+, 10^2\Sigma^+$ and $4^2\Pi$ obtained by Magnier and Frécon, are found to be repulsive whereas they are attractive when *ab-initio* methods are used.

To clarify the origin of such a disagreement, in this work, the $NaLi^+$ cation is re-investigated within the framework of the model potential approach. Adiabatic energies and corresponding molecular spectroscopic constants of states dissociating up to the limit Li^++Na(4d) are computed. A good agreement with the previous *ab-initio* calculations is observed.

Keywords: model potential, *$NaLi^+$*, *ab-initio*, adiabatic energies, molecular spectroscopic constant

1. Introduction

For the calculation of potential energy surfaces, most *ab-initio* techniques make use of Gaussian-type orbitals basis functions. In such a basis set, matrix

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Email addresses: `djamal.rabli@gmail.com` (Djamal Rabli), `ronald_mccarroll@upmc.fr` (Ronald McCarroll)

elements involving the electron-electron repulsion terms in the electronic Hamiltonian can be calculated analytically. On the other hand, such matrix elements in a Slater-type basis involve a numerical integration. However, for certain types of problems, a Slater-type basis does have certain particular virtues for the description of long-range interactions involving excited Rydberg states. For such states, the passive electrons may be represented by a model potential, designed to reproduce the experimental energies of the interacting atoms or ions. Molecules having only effective active electron provide a way to test the effectiveness of model potential methods for the calculation of excited electronic states, for which a Slater-type basis is well adapted. Such methods have proved to be very successful in providing an accurate description of avoided crossings of energy curves of excited adiabatic states. In practice, there are two types of systems which are amenable to the use of model potential techniques, namely the alkali molecular ions and the alkali-rare gas systems, both of which involve one active electron . Typical homo-nuclear alkali molecular ions such as Li_2^+, Na_2^+, K_2^+,. . . , and hetero-nuclear species such as LiNa^+, NaK^+, LiK^+,. . . , have been the subject of several extensive studies [3, 4, 5, 6, 7, 8, 9]. Typical alkali-rare gas, such as Na-He , Na-Ne , Na-Xe require a special treatment since in order to take account of the Pauli principle, it is necessary to preclude the active electron from the closed shell implicitly [10, 11]. An extensive review of more recent work has been presented by Ben Salem et al. [12].

In this paper, we will be concerned with the LiNa^+ molecular ion. From the experimental prespective, direct measurements of crossed-beam reaction rate coefficients for the production of NaLi^+ ions, have been reported by Johnson et al. [13]. Several other experimental studies involving indirectly this molecular ion, have been motivated by the measurement of cross sections of charge transfer process which occurs in Li^+/Na collisions [14, 15, 16, 17, 18]. From the theoretical point of view, besides computation of charge transfer cross sections which has motivated several studies [19, 20, 21, 22, 23], theoretical determination of the adiabatic energy curves of the NaLi^+ ion, has also received considerable attention. Indeed, the ground state $X^2\Sigma^+$ of this system has been computed in Hartree-Fock approximation by Bertoncini et al. [24], while the first systematic calculation of both the ground and excited states was carried out by Magnier and Frécon [2] using a model potential originally proposed by Klapisch [25] to describe the interaction of the valence electron with the lithium and sodium cores. Results were presented of the first eighteen low-lying molecular states (ten Σ^+, six Π and two Δ).

A little later, Berriche [1] developed a method combining *ab-initio* methods together with a non-empirical pseudo-potential to describe the Li^+ and Na^+ cores and taking into account the core-valence correlation as a correction. This method was used to calculate the adiabatic energies of the ground $X^2\Sigma^+$ state and of all the excited molecular states dissociating up to the Na(4d)+Li^+ limit. Subsequently, Khelifi et al. [26], following the formalism of Foucrault et al. [27] reproduced the spectroscopic constants of both, the NaLi alkali dimer and the $NaLi^+$ cation.

While different experimental and theoretical results show a global agreement for the $X^2\Sigma^+$ ground state, the lack of experimental data for the excited states of the $NaLi^+$ system makes it difficult to reach a final conclusion. However, there are significant disagreements between some of the theoretical results. Comparison between the *ab-initio* data [1, 26] and those of Magnier and Frécon [2] based on model potential techniques, exhibit a significant number of serious disagreement concerning several excited states. Some states are found to be repulsive by Magnier and Frécon [2] but attractive when *ab initio* techniques are used. According to the model potential results [2], the molecular states $2^2\Sigma^+$, $4^2\Sigma^+$, $6^2\Sigma^+$, $8^2\Sigma^+$, $10^2\Sigma^+$ and $4^2\Pi$ states do not exhibit any energy minimum whereas a well pronounced energy minimum is observed for these states in the *ab-initio* approach [1].

Bearing in mind that the disagreement between the *ab-initio* [1, 26] and the model potential results [2] occurs for states for which the energy minimum occurs at large equilibrium distances ($14 < R_e < 44$ a.u), where model potential methods are expected to provide an accurate description of the system, in the present work we re-investigate the $NaLi^+$ system using the model potential of Klapisch [25], previously employed by Magnier and Frécon [2]. We aim to clarify the origin of these existing disagreements: either due to a numerical artifact, or more seriously to some unknown limitation of either the *ab-initio* or model potential methods.

Except where stated, atomic units will be used throughout.

2. Theory

The interaction of the electron of valence with the closed shells, $Li^+(1s^2)$ and $Na^+(2p^6)$ cores, is described by model potentials $V^{Na/Li}_{model}$ previously used in the work by Magnier and Frécon [2] and originally proposed by Klapisch [25] in the form:

$$V_{model}(r) = -\frac{q}{r} - \frac{Z-1}{r}(e^{-\alpha_1 r} + \beta r e^{-\alpha_2 r}), \tag{1}$$

where r denotes the radial distance of the electron form the nucleus, q the ionic core charge and Z the atomic number. The set of parameters (α, β) shown in Tab.2,

Table 1: Comparison of calculated and experimental energy levels of the Na atom in a.u.

Level	Present work	[1]	[2]	Exp[28]
Li(2s)+Na$^+$	0.0000000	0.0000000	0.0000000	0.0000000
Li$^+$+Na(3s)	0.0092790	0.0092820	0.0093060	0.0092840
Li(2p)+Na$^+$	0.0679080	0.0679140	0.0679380	0.0679070
Li$^+$+Na(3p)	0.0866030	0.0865920	0.0865500	0.0865940
Li(3s)+Na$^+$	0.1238130	0.1239860	0.1238400	0.1239600
Li$^+$+Na(4s)	0.1264450	0.1265580	0.1264720	0.1265630
Li(3p)+Na$^+$	0.1407930	0.1409090	0.1408340	0.1409060
Li$^+$+Na(3d)	0.1422030	0.1422070	0.1421810	0.1422050
Li(3d)+Na$^+$	0.1425490	0.1425500	0.1425750	0.1425360
Li$^+$+Na(4p)	0.1470870	0.1472120	0.1471290	0.1472070
Li(4s)+Na$^+$	0.1594310	0.1595390		0.1595270
Li$^+$+Na(5s)	0.1604810	0.1605610		0.1605570
Li(4p)+Na$^+$	0.1659840	0.1661870		0.1661680
Li$^+$+Na(4d)	0.1665060	0.1667330		0.1667000

	q	Z	α_1	α_2	β
Li	1	3	7.90875	3.90006	1.0321
Na	1	11	7.88747	2.69155	2.354102

Table 2: Klapisch model potential parameters [25]

has been optimised such that the eigenvalues of the model atomic Hamiltonian

$$H_{model} = T + V_{model}, \tag{2}$$

where T is the kinetic energy operator, reproduce the experimental energies of the ground and the first few excited states of the corresponding ion, Li$^+$ and Na$^+$ in the present study.

Fixing the lithium and sodium cores at A and B positions respectively as shown in Figure 1, the NaLi$^+$ molecular cation is then treated as a set of two closed shells Li$^+$(1s^2) and Na$^+$(2p^6) cores and a single active electron moving in the field created by the two ionic cores, whose position is described in the Born-

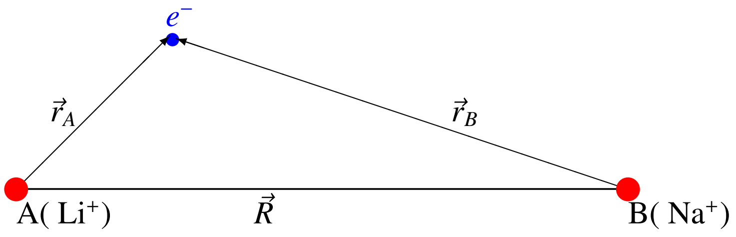

Figure 1: Relative coordinates for the active electron.

Oppenheimer approximation [34], by the electronic Hamiltonian

$$H_e = T + V^{Li^+}_{model}(r_A) + V^{Na^+}_{model}(r_B) + U_{core}, \tag{3}$$

where T denotes the electronic kinetic energy operator, r_A and r_B the radial distances of the active electron from the cores Li$^+$ and Na$^+$ respectively. Since we are concerned with intermediate and large internuclear distances only (R ≥ 4 a.u), U_{core} in previous equation (3), is mainly the nuclei repulsion modified by polarization terms namely:

$$U_{core} = \frac{q_{Li}.q_{Na}}{R} - \frac{\alpha^{Li}_d + \alpha^{Na}_d}{2R^4} - \frac{\alpha^{Li}_q + \alpha^{Na}_q}{2R^6}, \tag{4}$$

where q$_{Li}$ = q$_{Na}$ =1 denotes the ionic core charge, α_d and α_q are dipole and quadrupolar polarizabilities, respectively. In the present study, as in the work by Magnier and Frécon [2], we have used $\alpha^{Li}_d = 0.1915$ a.u [29], $\alpha^{Li}_q = 0.0156$ a.u [31] for lithium, and $\alpha^{Na}_d = 0.9965$ a.u [32] , $\alpha^{Na}_q = 0.376$ a.u [32] for sodium.

The spectrum of the effective Hamiltonian H$_e$ defined in equation (3) is determined by conventional variational techniques, using a basis set of Slater-type orbitals f$_{sto}$, expressed in prolate spheroidal coordinates $\lambda \in [1, \infty], \mu \in [-1, 1]$ and , $\phi \in [0, 2\pi]$ where

$$\lambda = \frac{1}{2R}(r_A + r_B), \qquad \mu = \frac{1}{2R}(r_A - r_B), \qquad \phi, \tag{5}$$

is the azimuthal angle.

In this prolate spheroidal coordinates system, the basis functions of Slater-type orbitals take the form:

$$\langle \lambda, \mu, \phi \mid f_{sto} \rangle = A[(\lambda^2 - 1)(1 - \mu^2)]^{\frac{\Lambda}{2}} \lambda^l \mu^k e^{-\frac{R}{2}\zeta(\lambda+\epsilon\mu)} e^{im\phi}, \tag{6}$$

where A denotes a normalisation factor, ϵ a parameter that takes the values ±1 depending on whether the orbital is centred on lithium or sodium cores, (l, k) integers, ζ a variational parameter describing the decay of the orbital, m the projection of the electronic angular momentum on the z-axis (coinciding with **R**) and $\Lambda = | m | = 0, 1, 2, \ldots$ for Σ^+, Π and Δ molecular states respectively.

3. Results

We have computed the adiabatic potential energies of the attractive ground state dissociating into a sodium ion Na^+ and a lithium atom in its ground state Li(2s), and of the manifold of excited states correlated in the asymptotic region to Na^++Li($1s^2$,nl), nl=2p, 3s, 3p, 3d, 4s, 4d and Li^++Na($2p^6$,nl), nl=3s, 3p, 4s, 3d, 4p, 5s, 4d.

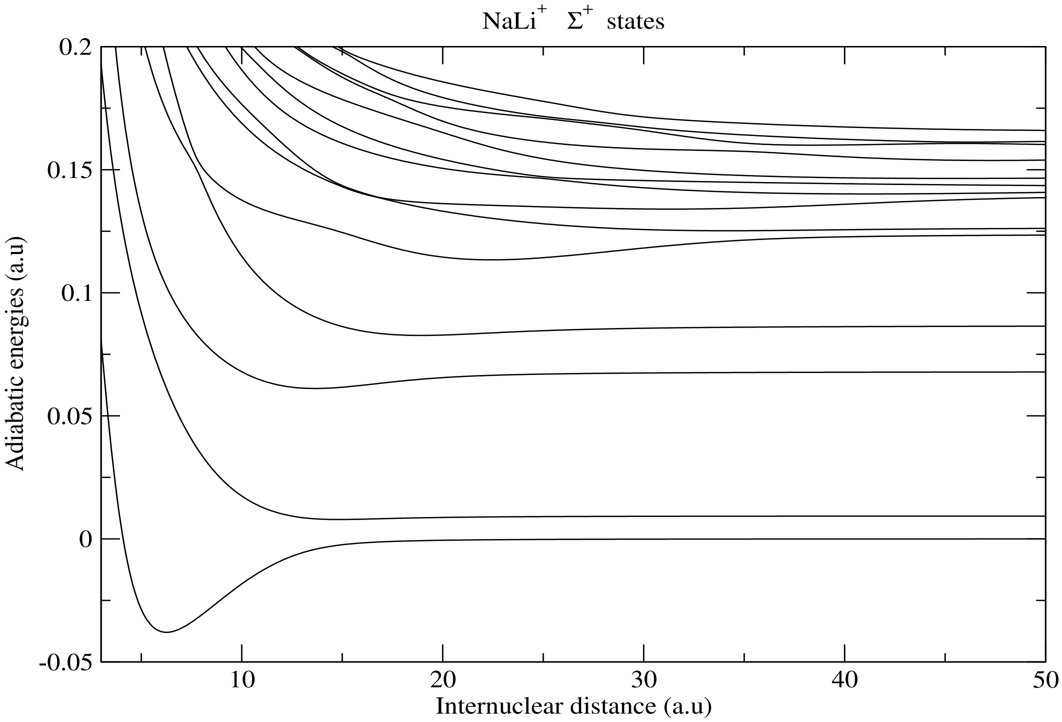

Figure 2: $NaLi^+$ potential energy curves of the $^2\Sigma^+$ states, given with respect to the ground state dissociation limit.

Table 3: Spectroscopic constants for ${}^2\Sigma^+$ states, R_e in a.u, D_e, ω_e, $\omega_e\chi_e$, B_e and T_e in cm^{-1}.

State	R_e	D_e	T_e	ω_e	$\omega_e\chi_e$	B_e	Reference
$X^2\Sigma^+$	6.26	8331		194.88	1.140	0.286	Present work
	6.37	8061		192.98	1.11	0.278607	Theory [1]
	6.35	7988		192.04			Theory [2]
	6.29	8155					Theory [26]
	6.35	8115		193	1.09	0.277	Theory [30]
		7985±242					Exp [33]
$2^2\Sigma^+$	14.83	307	10061	37.009	1.116	0.051	Present work
	14.90	294	9805	36.39	1.51	0.050840	Theory [1]
		Repulsive					Theory [2]
	14.94	295					Theory [26]
$3^2\Sigma^+$	13.65	1488	21745	57.961	0.564	0.060	Present work
	13.65	1423	21543	58.14	0.21	0.060663	Theory [1]
							Theory [2]
	13.57	1414					Theory [26]
$4^2\Sigma^+$	18.90	867	26476	38.139	0.419	0.031	Present work
	18.94	847	26219	32.54	13.76	0.031677	Theory [1]
		Repulsive					Theory [2]
	19.12	806					Theory [26]
$5^2\Sigma^+$	22.43	2289	33215	39.814	0.173	0.022	Present work
	22.41	2262	33011	41.12	0.33	0.022492	Theory [1]
	22.43	2300	32879	40.00			Theory [2]
	22.47	2194					Theory [26]
$6^2\Sigma^+$	34.16	270	35812	14.637	0.198	0.010	Present work
	34.24	265	35575	13.59	4.09	0.009606	Theory [1]
		Repulsive					Theory [2]
	34.72	165					Theory [26]
$7^2\Sigma^+$	31.35	1490	37741	17.135	0.050	0.011	Present work
		Repulsive					Theory [1]
		Repulsive					Theory [2]
	30.32	980					Theory [26]
$8^2\Sigma^+$	41.18	444	39091	11.410	0.073	0.007	Present work
	37.47	375	38896	43.29	13.00	0.008025	Theory [1]
		Repulsive					Theory [2]

	40.76	112					Theory [26]
$9^2\Sigma^+$		Repulsive					Present work
		Repulsive					Theory [1]
		Repulsive					Theory [2]
		Repulsive					Theory [26]
$10^2\Sigma^+$	45.14	138	40475	8.225	0.122	0.006	Present work
	44.95	127	40242	2.83	19.36	0.005090	Theory [1]
		Repulsive					Theory [2]
	44.20	16					Theory [26]
$11^2\Sigma^+$	47.33	1243	42078	15.471	0.048	0.005	Present work
		Repulsive					Theory [1]
	42.99	74					Theory [26]
$12^2\Sigma^+$	62.64	230	43322	6.375	0.044	0.003	Present work
	62.05	201	44103	6.97	0.03	0.002933	Theory [1]
	45.01	10					Theory [26]
$13^2\Sigma^+$	46.19	1048	43713	21.642	0.112	0.005	Present work
	33.91	488	44138	41.99	18.99	0.009791	Theory [1]
		Repulsive					Theory [26]
$14^2\Sigma^+$	68.71	501	44371	5.499	0.015	0.0024	Present work
		Repulsive					Theory [1]
		Repulsive					Theory [26]

3.1. Σ^+ states

Graphics showing our adiabatic potential energies curves for the $^2\Sigma^+$ states, are presented in Fig.2, for internuclear separations up to 50 a.u while comparison of the obtained spectroscopic constants with available values resulting from different approaches is shown in Table 3.

For the $X^2\Sigma^+$ ground state, present calculations yield a dissociation energy D_e =8331 cm^{-1} and an equilibrium distance R_e=6.26 a.u. These values may be compared to the *ab-initio* results of Berriche [1], D_e=8061 cm^{-1} and R_e=6.37 a.u, and to those of Khelifi et al. [26], D_e=8155 cm^{-1} and R_e=6.29 a.u. Our vibration constants ω_e=194.88 cm^{-1} and $\omega_e\chi_e$= 1.14 cm^{-1}, also compare well to the *ab-initio* ones [1], ω_e=192.98 cm^{-1} and $\omega_e\chi_e$=1.11 cm^{-1}, however due to the nonavailability of the experimental values, we simply mention that our dissociation energy which is slightly greater than other available theoretical values, compares favourably to the experimental value [33] predicted in the range

D_e=7985±242cm^{-1}.

On the other hand, our potential energy curve relative to the $2^2\Sigma^+$ state exhibits an energy minimum occurring at an equilibrium internuclear distance R_e=14.83 a.u, with a corresponding dissociation energy D_e=307 cm^{-1} and vibration constants ω_e=36.984 cm^{-1} and $\omega_e\chi_e$=1.115 cm^{-1}. Therefore, contrary to the conclusion of Magnier and Frécon [2], and as predicted by previous *ab-initio* methods [1, 26], present study confirms the attractive behaviour of the $2^2\Sigma^+$ state.

For the $3^2\Sigma^+$ state, our calculations give a dissociation energy D_e=1488 cm^{-1}, an equilibrium distance R_e= 13.65 a.u and vibration constants ω_e=57.961 cm^{-1} and $\omega_e\chi_e$=0.564 cm^{-1}. As shown in Table 3, these values are in good agreement with those of Berriche [1] resulting from an *ab-initio* calculation.

On the other hand, for the $4^2\Sigma^+$ state, contrary to the conclusion of Magnier and Frécon [2], the present study clearly indicates that a such state is attractive with a dissociation energy D_e=867 cm^{-1}, an equilibrium distance R_e=18.90 a.u and vibration constants ω_e = 38.139 cm^{-1} and $\omega_e\chi_e$= 0.419 cm^{-1}. While those new results agree with the *ab-initio* ones of Berriche [1], our vertical excitation T_e= 26476 cm^{-1}, remains about 300 cm^{-1} greater than the *ab-initio* value. This is due to our ground state which seems to be about 300 cm^{-1} deeper than the value predicted by *ab-initio* methods.

For the $5^2\Sigma^+$ state which has also been generated in the present work, our results show that this state has an equilibrium distance R_e=22.43 a.u and a dissociation energy D_e=2289 cm^{-1}. As shown in Table 3, those values compare well to the *ab-initio* results of Berriche [1], D_e=2262 cm^{-1}, R_e=22.41 a.u and to the ones of Khelifi et al. [26], D_e=2194 cm^{-1} and R_e=22.47 a.u.

As previously mentioned, the $6^2\Sigma^+$ state has been a subject of disagreement when comparing *ab-initio* [1] and model potential results [2], contrary to the claims of Magnier and Frécon [2], present results show that the $6^2\Sigma^+$ state is attractive with a dissociation energy D_e=270 cm^{-1} and an internuclear equilibrium distance R_e=34.16 a.u. Those values may be compared to the *ab-initio* ones of Berriche [1], D_e=265 cm^{-1}, R_e=34.24 a.u and to the ones of Khelifi et al. [26], D_e=165 cm^{-1} and R_e=34.72 a.u.

Equally, the analysis of our potential energy curves shows that the $7^2\Sigma^+$ state correlated to Na^++Li(3p) in the asymptotic limit, has a well pronounced energy minimum occurring at an equilibrium distance R_e= 31.35 a.u with a dissociation energy D_e=1490 cm^{-1}. According to the *ab-initio* results of Kheliifi et al. [26] this state is also attractive with D_e=980 cm^{-1}, while according to results of Berriche [1] and those of [2] the $7^2\Sigma^+$ state is purely repulsive.

For the $8^2\Sigma^+$ correlated in the asymptotic limit to Li^++Na(3d) and which also has been subject of disagreement when comparing previous *ab-initio* [1] and model potential [2] results, contrary to the conclusion of Magnier and Frécon [2], our $8^2\Sigma^+$ is an attractive molecular state with an equilibrium distance R_e= 41.18 a.u and a dissociation energy D_e= 444 cm^{-1}. Those new values may be compared to the *ab-initio* ones of Berriche [1] D_e=375 cm^{-1} and R_e=37.47 a.u and to those of Khelifi et al. [26], D_e=112 cm^{-1} and R_e=40.76 a.u.

On the other hand, for the $9^2\Sigma^+$ state, correlated to Li(3d)+Na^+ in the asymptotic limit, as predicted by previous works [1, 2, 26] our study indicates that the $9^2\Sigma^+$ state is purely repulsive.

While previous model potential results [2] concluded that the $10^2\Sigma^+$ state is repulsive, our work shows that this state has an attractive behaviour with an equilibrium distance R_e= 45.14 a.u and a corresponding dissociation energy D_e=138 cm^{-1}. As shown in Table 3, those new values are in agreement when they are compared to the ones issued from an *ab-initio* study [1], D_e=127 cm^{-1} and R_e= 44.95 a.u.

The set of excited states $11^2\Sigma^+$, $12^2\Sigma^+$, $13^2\Sigma^+$ and $14^2\Sigma^+$ have not been included in the previous work by Magnier and Frécon [2] and are generated for the first time in a study based on a model potential approach. For the $11^2\Sigma^+$, our study yields an equilibrium distance R_e= 47.33 a.u with a corresponding dissociation energy D_e=1243 cm^{-1}, however a such state has been found repulsive in the *ab-initio* study of Berrihe [1], but attractive R_e= 42.99 a.u in the work of Khelifi et al. [26].

On the other hand, the present study shows that the $12^2\Sigma^+$ state correlated to Li^++Na(5s) in the dissociation limit has a well pronounced minimum of 230 cm^{-1} occurring at an equilibrium distance R_e= 62.64 a.u. Those values are compared to the *ab-initio* results [1], D_e=201 cm^{-1} and R_e= 62.05 a.u. Equally, our our vibration constants ω_e=6.375 cm^{-1} and $\omega_e\chi_e$=0.044cm^{-1} compare favourably to the *ab-initio* values [1], ω_e=6.97 cm^{-1} and $\omega_e\chi_e$=0.03cm^{-1}.

Our study also shows that the potential energy curve for the $13^2\Sigma^+$ state, has a minimum occurring at an equilibrium distance R_e= 46.19 a.u, and a dissociation energy 1048 cm^{-1}. Since those values remain different from the *ab-initio* results [1], R_e= 33.91 a.u and D_e=488 cm^{-1}, it is not obvious to reach an accurate conclusion and certainly an experimental investigation focusing on a such state will be of great interest.

Finally, as shown in Table 3, our $14^2\Sigma^+$ state exhibits an energy minimum occurring at a very large equilibrium distance R_e=68.71 a.u with a corresponding dissociation energy D_e=501 cm^{-1}, whereas a such state has been found attractive when *ab-initio* methods [1, 26] are employed

3.2. Π *states*

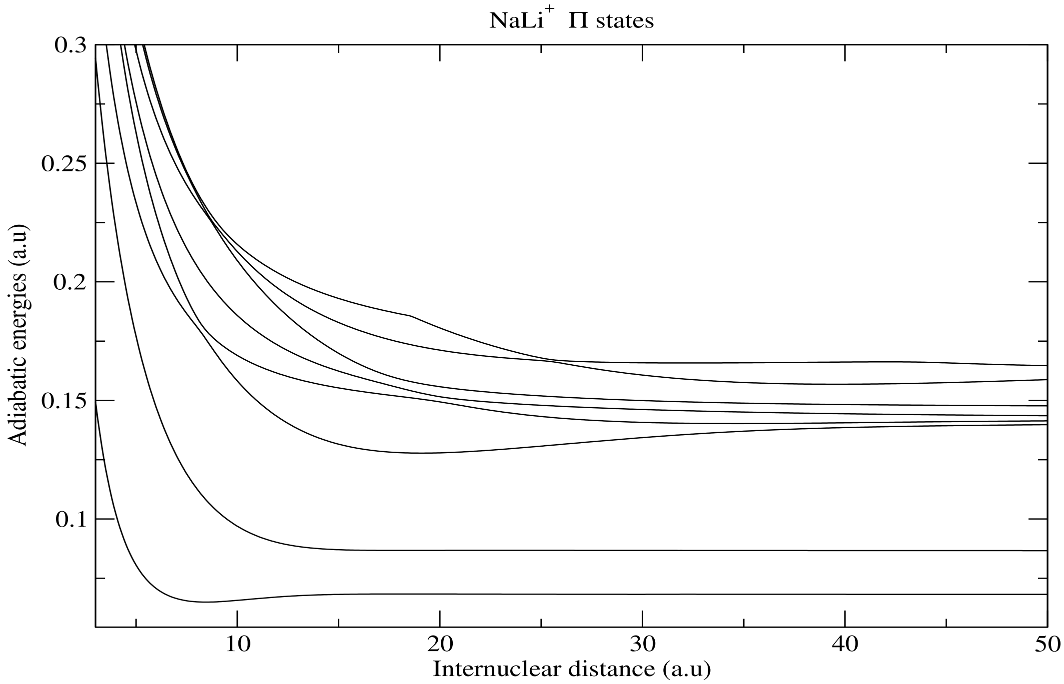

Figure 3: NaLi$^+$ potential energy curves of the $^2\Pi$ states, given with respect to the ground state dissociation limit.

The obtained adiabatic potential energies curves for the $^2\Pi$ states, are plotted in Fig.3 for internuclear separations up to 50 a.u, while comparison of the corresponding spectroscopic constants with available values resulting from different approaches is shown in Table 4.

For the $1^2\Pi$ state correlated in the dissociation limit to Na$^+$+Li(2p), present study yields a dissociation energy D_e=663 cm^{-1} and an equilibrium distance R_e= 8.46 a.u. Those may be compared to values issued from an *ab-initio* approach [1], D_e=496 cm^{-1} and R_e= 8.53 a.u and to those exploiting model potential approach [2] D_e=614 cm^{-1} and R_e= 8.56 a.u. As indicated in Table 4, our vibration constants ω_e = 67.271 cm^{-1} and $\omega_e\chi_e$=1.704 cm^{-1}, also compare favourably to the *ab-initio* values [1], ω_e = 68.70 cm^{-1} and $\omega_e\chi_e$=1.40 cm^{-1}.

On the other hand, as shown in Fig. 4, the analysis of the potential energy curve of the $1^2\Pi$ state at intermediate internuclear separations, indicates the existence of a potential barrier, located at an internuclear distance around 18 a.u with a maximum height of 62.55 cm^{-1}.

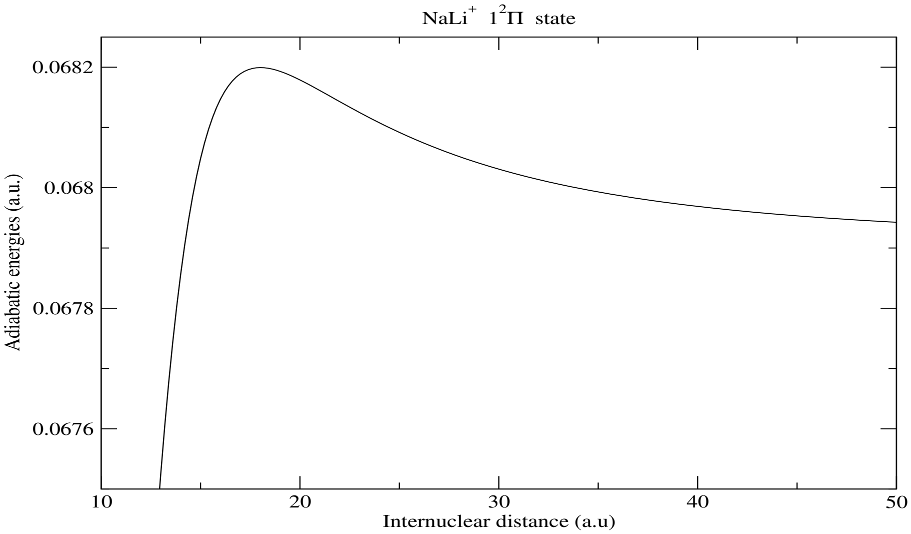

Figure 4: Shape of the potential barrier in the $1^2\Pi$ state. Energies are given with respect to the ground state dissociation limit.

Table 4: Spectroscopic constants for $^2\Pi$ states, R$_e$ in a.u, D$_e$, ω_e, $\omega_e\chi_e$, B$_e$ and T$_e$ in cm^{-1}.

State	R$_e$	D$_e$	T$_e$	ω_e	$\omega_e\chi_e$	B$_e$	Reference
$1^2\Pi$	8.46	663	22572	67.271	1.704	0.156	Present work
	8.53	496	22471	68.70	1.40	0.155188	Theory [1]
	8.56	614	22282	58.24			Theory [2]
	8.50	519.3					Theory [26]
$2^2\Pi$	17.98	-26.95	27366	10.479	-1.018	0.0346	Present work
	Repulsive						Theory [1]
	Repulsive						Theory [2]
	Repulsive						Theory [26]
$3^2\Pi$	19.09	2864	36370	38.264	0.129	0.0307	Present work
	19.35	2667	36319	37.27	0.13	0.030175	Theory [1]
	19.09	2863	36020	38.34			Theory [2]
	19.20	2432.8					Theory [26]
$4^2\Pi$	34.64	423	39106	12.927	0.098	0.009	Present work
	34.76	398	38872	7.12	42.57	0.009550	Theory [1]
	41.28	422	38849	6.76	42.57	0.009550	Theory [1]
	Repulsive						Theory [2]

	34.3	268					Theory [26]
$5^2\Pi$	Repulsive						Present work
	Repulsive						Theory [1]
	Repulsive						Theory [2]
	Repulsive						Theory [26]
$6^2\Pi$	Repulsive						Present work
	Repulsive						Theory [1]
	Repulsive						Theory [2]
	Repulsive						Theory [26]
$7^2\Pi$	39.51	2035	42749	16.943	0.0352	0.007	Present work
	46.01	1098	43442	71.71	10.08	0.006647	Theory [1]
	37.7	479					Theory [26]
$8^2\Pi$	59.70 (outer)	505	44318	6.895	0.023	0.003	Present work
	32.21 (inner)	176	44715	10.959	0.169	0.011	Present work
	79.30	108	44524	14.61	0.10	0.011436	Theory [1]
	118.38	81	44551	1.92	0.10	0.011436	Theory [1]
	Repulsive						Theory [26]

For the $2^2\Pi$ state, correlated to Li^+ + Na(3p) in the asymptotic limit, our potential energy curve is shown in Fig. 5. Present results indicate that this state has a very weak energy minimum of 26.95 cm^{-1} occurring at an equilibrium distance of 17.98 a.u, while according to previous studies employing both methods, *ab-initio* and model potential [2, 1], the $2^2\Pi$ state is purely repulsive.

For the $3^2\Pi$ state, present study shows that the potential energy curve relative to this state has an energy minimum occurring at an equilibrium distance R_e = 19.09 a.u with a corresponding dissociation energy D_e=2864 cm^{-1} and vibration constants ω_e = 38.264 cm^{-1} and $\omega_e\chi_e$=0.129 cm^{-1} Those values to be compared to the *ab-initio* results [1], R_e = 19.35 a.u D_e=2667 cm^{-1}, ω_e = 37.27 cm^{-1} and $\omega_e\chi_e$=0.139 cm^{-1}.

On the other hand, our $4^2\Pi$ state which has been a subject of disagreement when comparison of previous *ab-initio* results [1] and model potential ones [2] is made, contrary to the claims of Magnier and Frécon [2], a such state is attractive with a dissociation energy D_e=423 cm^{-1}, and an equilibrium distance R_e =34.64 a.u. These results are in agreement with what have been predicted by previous *ab-initio* studies [1], giving for dissociation energy D_e= 398 cm^{-1} and for equilibrium distance R_e =34.76 a.u.

For the $5^2\Pi$ and $6^2\Pi$ states, the analysis of our potential energies curves does

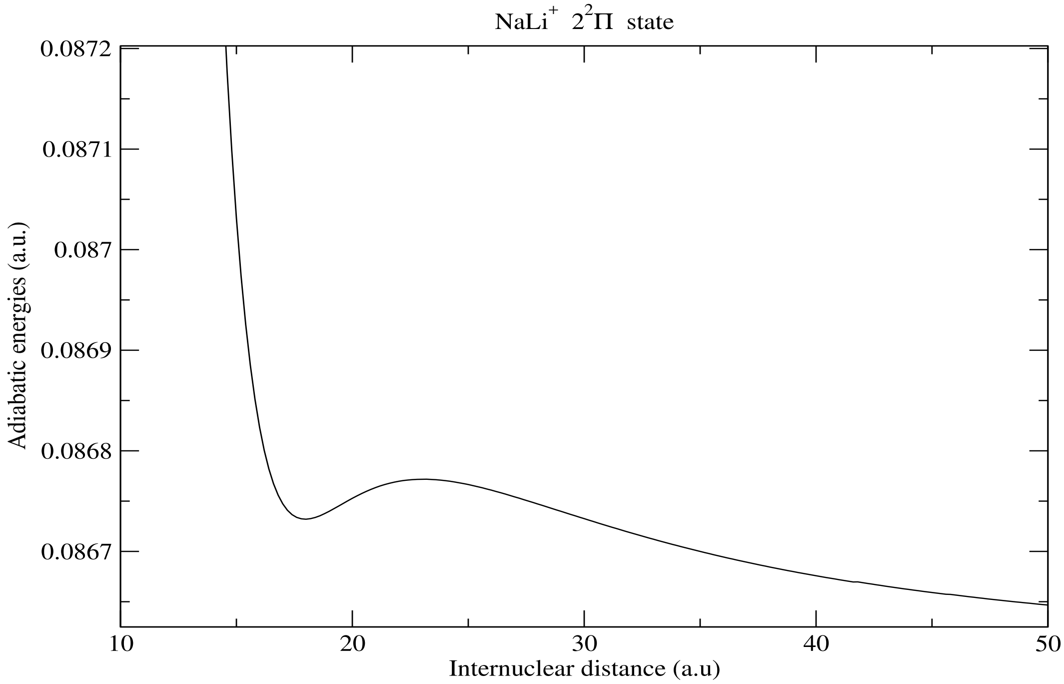

Figure 5: NaLi$^+$ potential energy curves of the $2^2\Pi$ state. Energies are given with respect to the ground state dissociation limit.

not show any energy minimum therefore, these states are repulsive, as predicted by other studies based on *ab-initio* methods [1, 26] and model potential approach [2], as well.

Finally we mention that our excited molecular states 7 $^2\Pi$ and 8 $^2\Pi$ computed in the present study, have been found to be attractive as predicted by *ab-initio* methods [1]. However, as shown in Table 4, values of our spectroscopic constants remind different from the *ab-initio* ones.

3.3. Δ states

Our potential energy curves for the $^2\Delta$ symmetry are plotted in Fig. 6 for different internuclear distances up to 50 a.u, and the corresponding spectroscopic constants are compared to available data issued from different methods in Table 5.

The $1^2\Delta$ state, correlated in the asymptotic limit to Li$^+$+Na(3d), exhibits an energy minimum at an equilibrium distance R_e=17.89 a.u, with a corresponding dissociation energy D_e= 307 cm^{-1}. These values, as shown in Table 5, compare well to those of Magnier and Frécon [2], but a difference around 250 cm^{-1} in dissociation energy is observed when comparison is made with *ab-initio* results [1]. From Table 5, it is also easy to see that our frequencies ω_e=21.572 cm^{-1} and $\omega_e\chi_e$=0.386 cm^{-1} and vertical excitation energy T$_e$ =39252 cm^{-1}, compare favourably to the *ab-initio* results [1] ω_e=18.48 cm^{-1}, $\omega_e\chi_e$=0.35 cm^{-1} and T$_e$ =39216 cm^{-1}.

On the other hand, our study shows that the 2 $^2\Delta$ state correlated in the asymptotic region to Na$^+$+Li(3d), is a repulsive state, as predicted by previous studies of Magnier and Frécon [2] based on model potential and those of Berriche and Khelifi [1, 26] using an *ab-initio* approach.

For the 3$^2\Delta$ state correlated to Li$^+$+Na(4d), present calculations yield a dissociation energy D$_e$=912 cm^{-1} and an equilibrium distance R$_e$= 31.75 a.u. Those values may be compared to the *ab-initio* ones [1] D$_e$=522 cm^{-1} and R$_e$= 31.10 a.u. If both calculations are giving a large equilibrium distance around 31 a.u, our dissociation energy well is about 400 cm^{-1} deeper.

Table 5: Spectroscopic constants for $^2\Delta$ states, R$_e$ in a.u, D$_e$, ω_e, $\omega_e\chi_e$, B$_e$ and T$_e$ in cm^{-1}.

State	R$_e$	D$_e$	T$_e$	ω_e	$\omega_e\chi_e$	B$_e$	Reference
1$^2\Delta$	17.89	307	39252	21.752	0.386	0.035	Present work
	19.59	57	39216	18.48	0.35	0.029415	Theory [1]
	17.97	340	38900	22.0			Theory [2]
	20.3	110.8					Theory [26]
2$^2\Delta$	Repulsive						Present work
	Repulsive						Theory [1]
	Repulsive						Theory [2]
	Repulsive						Theory [26]
3$^2\Delta$	31.75	912	43477	17.123	0.080	0.011	Present work
	31.10	522	44110	14.15	8.43	0.011596	Theory [1]
	29.8	234					Theory [26]

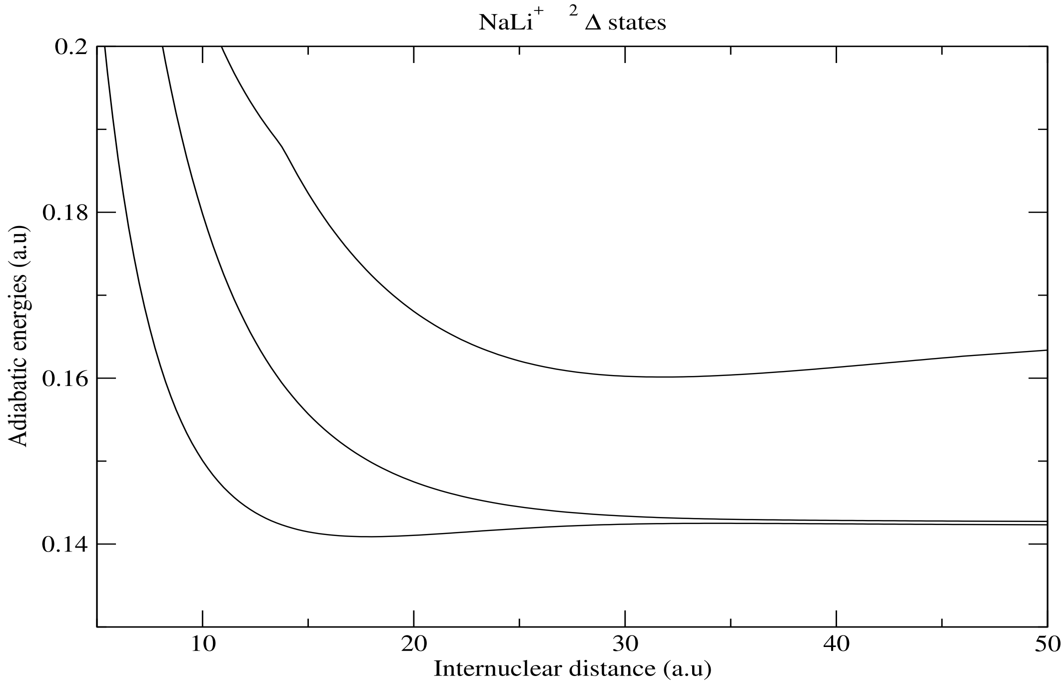

Figure 6: NaLi$^+$ potential energy curves of the $^2\Delta$ states, given with respect to the ground state dissociation limit.

4. Avoided crossing

A simple analysis of our potential energy curves shows the presence of an important number of avoided crossings between adjacent adiabatic states belonging to the same molecular symmetry. It is well known that the internuclear distance R_c of the pseudo-crossing and the corresponding energy gap ΔE_c are relevant to charge transfer process, and can be used to estimate cross sections via Landau-Zener approximation [35].

Our avoided crossing parameters obtained in the present study, are compared with values issued from different methods in Table 6. Good agreement with previous model potential and *ab-initio* [1, 2] results is observed. Our crossing radius for $5/6^2\Sigma^+$ and $6/7^2\Sigma^+$ crossings which have been omitted in the study of Magnier and Frécon [2], also compare favourably to the *ab-initio* results [1]. However a difference in R_c values, between our results and *ab-initio* ones [1] seems to become more important for crossings involving excited states.

Table 6: Avoided crossing parameters (R_c, ΔE_c)

	Present work		*Ab-initio*[1]	Model potential [2]
Avoided crossing	ΔE_c(a.u)	R_c(a.u)	R_c(a.u)	R_c(a.u)
$4^2\Sigma^+ - 5^2\Sigma^+$	$4.60\ 10^{-3}$	7.75	7.73	7.75
$5^2\Sigma^+ - 6^2\Sigma^+$	$4.32\ 10^{-3}$	4.18	4.29	4.25
$5^2\Sigma^+ - 6^2\Sigma^+$	$1.83\ 10^{-2}$	15.77	15.61	
$6^2\Sigma^+ - 7^2\Sigma^+$	$7.42\ 10^{-3}$	8.07	7.86	
$6^2\Sigma^+ - 7^2\Sigma^+$	$1.09\ 10^{-4}$	16.73	16.02	16.5
$7^2\Sigma^+ - 8^2\Sigma^+$	$1.27\ 10^{-2}$	11.20	11.4	
$8^2\Sigma^+ - 9^2\Sigma^+$	$1.35\ 10^{-3}$	7.54	7.52	7.5
$8^2\Sigma^+ - 9^2\Sigma^+$	$7.15\ 10^{-4}$	25.06	24.59	25
$9^2\Sigma^+ - 10^2\Sigma^+$	$5.80\ 10^{-3}$	10.92	10.82	
$10^2\Sigma^+ - 11^2\Sigma^+$	$6.71\ 10^{-4}$	6.66	6.7	
$10^2\Sigma^+ - 11^2\Sigma^+$	$4.52\ 10^{-3}$	20.44	20.19	
$11^2\Sigma^+ - 12^2\Sigma^+$	$7.51\ 10^{-4}$	13.27	10.26	
$11^2\Sigma^+ - 12^2\Sigma^+$	$3.23\ 10^{-3}$	35.89	33.50	
$12^2\Sigma^+ - 13^2\Sigma^+$	$6.11\ 10^{-3}$	10.71	16.00	
$12^2\Sigma^+ - 13^2\Sigma^+$	$7.64\ 10^{-4}$	25.58	22.25	
$13^2\Sigma^+ - 14^2\Sigma^+$	$9.03\ 10^{-4}$	15.13	14.51	
$3^2\Pi^+ - 4^2\Pi^+$	$3.52\ 10^{-3}$	8.27	8.18	8.25
$4^2\Pi^+ - 5^2\Pi^+$	$2.18\ 10^{-3}$	20.01	19.59	20
$5^2\Pi^+ - 6^2\Pi^+$	$3.78\ 10^{-3}$	18.11	18.19	18.25
$6^2\Pi^+ - 7^2\Pi^+$	$6.06\ 10^{-4}$	8.69	8.34	
$7^2\Pi^+ - 8^2\Pi^+$	$8.36\ 10^{-4}$	25.51	29.75	

5. Conclusion

We have investigated the $NaLi^+$ cation using a model potential approach to compute the adiabatic potential energies and the molecular spectroscopic constants for the first low-lying, fourteen $^2\Sigma^+$, eight $^2\Pi$ and three $^2\Delta$ states, dissociating up to the Li^++Na(4d) limit.

A good agreement between the present results based on model potential approach and those issued from *ab initio* methods is observed. This is an indication that the model potential method remains efficient in providing accurate description of molecular systems involving one single active electron.

On the other hand, the disagreement mentioned above, between results based on *ab-initio* [1] methods and those obtained by previous model potential calculations [2], concerning the $2^2\Sigma^+$, $4^2\Sigma^+$, $6^2\Sigma^+$, $8^2\Sigma^+$, $10^2\Sigma^+$ and $4^2\Pi$ states, has been sorted out in the present work. Contrary to the conclusion of Magnier and Frécon [2], our model potential results show that the potential energy curves relative to these molecular states are attractive with a well pronounced energy minimum, as predicted by other studies exploiting *ab-initio* techniques.

6. References

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