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Theoretical investigation of the molecular structure and transition dipole moments of the NaK$^+$ low lying electronic states

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Abstract

The electronic structure and the spectroscopic constants of the low lying electronic states of the NaK$^+$ ionic molecule have been determined through using an ab initio approach involving a non-empirical pseudopotential for the Na and K cores and core valence correlation correction. The potential energy of nearly 26 electronic states of $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ symmetries has been calculated up to their dissociation limit Na(4d) + K$^+$ and Na$^+$ + K(6s). Their spectroscopic constants (R_e, D_e, T_e, ω_e, $\omega_e\chi_e$, and B_e) are derived and compared with the few available theoretical studies. A good agreement has been found for the ground state and few excited states with previous works. New potential energy curves were presented, for the first time, for the higher excited states. Numerous avoided crossing between electronic states of $^2\Sigma^+$, $^2\Pi$ symmetries have been localized and analyzed. Their existences are related to the charge transfer between the two ionic molecules Na$^+$K and NaK$^+$. Furthermore, we have determined the transition dipole moments for several states and analyzed the avoided crossings related to charge transfer between alkaline atoms.
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Keywords: Ab initio; NaK$^+$; Transition dipole moment; Avoided crossing

1. Introduction

Diatomic alkali molecules present probably the most understood diatomic molecules. They have been the subject of numerous theoretical and experimental investigations. This is due to the simplicity of such systems with no more than two valence electrons. Experimentally, they are relatively easy to be handled. In contrast, experimental information on heteronuclear ionic alkali diatomic molecules is quite scarce. This can be explained by the fact that the formation of AB$^+$ systems (A and B are alkali atoms) is dominated by the formation of A$_2^+$ and B$_2^+$ because of the difference of the melting points to produce A and B in vapor form. The absence of experimental data has limited the theoretical interest in studying the neutral and ionic

heteronuclear alkali dimers. The reduced number of valence electrons of such systems allowed high quality of ab initio calculations [1]. Several techniques have been used to study alkali dimers. Most of them have proposed to reduce the number of electrons to only valence electrons. The pseudopotentials or model potential have been used to replace the effect of core electrons on the valence electron. In the model potential calculations—which have been developed by Bottcher and Dalgarno [2]—the alkali cations are treated as a system with one electron under a potential to fit experimental atomic energy levels. The use of pseudopotentials for Na and K cores reduces the number of active electrons to only one valence electron. The SCF calculation produces the exact energy and the main source of errors corresponds to the basis-set limitations. Furthermore, we correct the energy by taking into account the core–core and core–electron correlation following the formalism of Foucrault et al. [3]. This formalism was used for several homonuclear and heteronuclear molecules such

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as Rb_2, RbCs, LiH, LiH^+, Li_2^+, $LiNa^+$, and LiK^+ and has proved efficiency.

Alkali and hydrogen alkali dimers form a prototype systems for investigation of non-adiabatic coupling [4–6], collision process radiative association and dissociation [7–9], diabatization and predissociation [6,10]. The spectroscopy of such systems has been extensively studied using high resolution methods [11]. In addition, the advances in the knowledge of ultralow temperature gases have induced recently a new interest in alkali dimer cations. Furthermore, the determination of accurate potential energy curves and transition dipole moments of alkali diatomic ionic or neutral systems constitutes the basic information for studying important physical problems such as photodissociation processes [12–14] and wave packet dynamics simulations [14,15]. To achieve all such aims, the determination of accurate electronic and spectroscopic data is an urgent need.

In spite of the relative simplicity of the NaK^+ system, most of the theoretical works [16–21] have been focused on the ground state. Müller and Meyer [17] have determined for NaK^+ the spectroscopic constants of only the ground state. In their work, the objective was to test the pseudopotential formalism at the SCF level for diatomic molecules, which have two and one valence electrons. Later, Valance et al. [21] have studied the ground and the first six exited states of $^2\Sigma^+$, $^2\Pi$ symmetries. Their potentials were calculated to a distance limit of 20 a.u., which did not permit them to well explore their potential wells. As a result, they found most of them repulsive. To the best of our knowledge, there are no experimental studies done on NaK^+ until now. However, the neutral molecule was extensively studied both experimentally [22–29] and theoretically [30–35]. A full study of the NaK^+ cation will be presented in this paper where the higher excited states are studied for the first time. Having only one active electron, the NaK^+ will be not only one of the simplest heteromolecular systems but also the computing time is going to be reduced. Very large basis sets for valence and Rydberg states for Na and K atoms were used. They have allowed once an accurate description for the highest excited states and the production of a large number of molecular states.

The present work follows our study on many diatomic systems, such as LiH [6], LiH^+ [36], $LiNa^+$ [37], LiK^+ [38], and triatomic systems such as LiH_2 [39,40] where we have used the same techniques. For all of the mentioned systems we have achieved a remarkable accuracy that showed the validity of this approach. The present calculation for NaK^+ cation system is expected to reach a similar accuracy since the main restriction in the accuracy of the calculation is only the basis-set limitation. We present a complete set of results including all Rydberg states. Our aim is to provide a systematic study of the electronic structure and the transition dipole moments of the alkali heteronuclear cations. That is to say to produce, for such systems, full and accurate electronic and spectroscopic data for further theoretical and experimental use.

In the next section, we briefly present the computational method. In Section 3, we present the potential energy curves and their spectroscopic constants for the ground and numerous excited states of $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ symmetries dissociating into Na(3s, 3p, 3d, 4s, 4p, 5s, 4d) + K^+ and Na^+ + K(4s, 4p, 5s, 3d, 5p, 4d, 6s). Section 4 is devoted to the avoided crossing between the electronic states, which are related to the charge transfer process between Na and K atoms. In Section 5, we present the transition dipole moments from X, 2, 3, and 4 $^2\Sigma$ states to higher excited states. Finally, we summarize our conclusion in Section 5.

2. Method of calculation

The Na and K atoms are treated as a one-electron system using the non-empirical pseudopotentials of Barthelat and Durand [41] in its semilocal form. For the simulation of the interaction between the polarizable Na^+ and K^+ cores with the valence electrons, a core polarization potential V_{CPP} is used according to the operatorial formulation of Müller et al. [42].

$$V_{CPP} = -\frac{1}{2} \sum_\lambda \alpha_\lambda f_\lambda \cdot f_\lambda.$$

The summation runs over all the polarizable cores λ with a dipole polarizability α. f_λ is the electric field created on center λ produced by valence electrons and all other cores.

$$f_\lambda = \sum_i \frac{\vec{r}_{i\lambda}}{r_{i\lambda}^3} F_l(r_{i\lambda}, \rho_\lambda) - \sum_{\lambda' \neq \lambda} \frac{\vec{R}_{\lambda'\lambda}}{R_{\lambda'\lambda}^3} Z_\lambda,$$

where $r_{i\lambda}$ is a core–electron vector and $R_{\lambda'\lambda}$ is a core–core vector.

According to the formulation of Foucrault et al. [3], the cutoff function $F_l(r_{i\lambda}, \rho_\lambda)$ is taken to be a function of l to consider differently the interaction of valence electrons of different spatial symmetry with core electrons.

$$F(r_{i\lambda}, \rho_\lambda) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} F_l(r_{i\lambda}, \rho_\lambda^l) |lm\lambda\rangle \langle lm\lambda|,$$

where $|lm\lambda\rangle$ is the spherical harmonic centered on λ. $F(r_{i\lambda}, \rho_\lambda^l)$ is the cutoff operator, expressed following the Foucrault et al. [3] formalism by a step function defined by

$$F(r_{i\lambda}, \rho_\lambda^l) = \begin{cases} 0 & r_{i\lambda} < \rho_\lambda, \\ 1 & r_{i\lambda} > \rho_\lambda. \end{cases}$$

It has a physical meaning of excluding the valence electrons from the core region for calculating the electric field. In Müller et al. [42] formalism, the cutoff function is unique for a given atom, generally adjusted to reproduce the first ionization potential. The different used cutoff parameters ρ_λ^l are reported in Table 1. They were optimized in order to reproduce the ionization potentials and the lowest valence s, p, d, and f one-electron states as deduced from the atomic data tables.

Table 1
l-dependent cutoff radii (in bohr) for Na and K atoms

l	Na	K
s	1.4423	2.067
p	1.625	1.905
d	1.5	1.96
f	1.5	1.96

Table 2
Asymptotic energy of the NaK$^+$ electronic states (cm^{-1})

Asymptotic limit	This work	Experimental [45]	ΔE
Na (3*s*) + K$^+$	0.00	0.00	0.00
Na (3*p*) + K$^+$	16967.61	16967.61	0.00
Na (4*s*) + K$^+$	25739.15	25739.80	0.65
Na (3*d*) + K$^+$	29173.71	29172.83	0.88
Na (4*p*) + K$^+$	30272.18	30270.65	1.53
Na (5*s*) + K$^+$	33201.95	33200.64	1.31
Na (4*d*) + K$^+$	34556.55	34548.87	4.68
K (4*s*) + Na$^+$	0.00	0.00	0.00
K (4*p*) + Na$^+$	13022.96	12985.17	37.79
K (5*s*) + Na$^+$	21017.98	21026.8	8.82
K (3*d*) + Na$^+$	21535.51	21534.42	1.09
K (5*p*) + Na$^+$	24750.81	24701.44	49.37
K (4*d*) + Na$^+$	27417.21	27397.01	20.20
K (6*s*) + Na$^+$	27451.88	27450.65	1.23

Fig. 1. Potential energy curves for the lowest 1–14 $^2\Sigma$ electronic states of NaK$^+$ dissociating into Na(3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*) + K$^+$ and Na$^+$ + K(4*s*, 4*p*, 5*s*, 3*d*, 5*p*, 4*d*, 6*s*).

For Na atom we used the same basis set of gaussian-type orbitals (GTOs) as in our previous work on LiNa$^+$ molecule [37]. For K atom we used the basis set of Magnier and Milié [43] which was built at first by Jeung and Ross [44] and developed by adding more diffuse orbital necessary for the description of highly excited states. The used core dipole polarizabilities of Na and K are, respectively, 0.993 and 5.354 a_0^3. The potential energy has been calculated using the standard chain of programs (PSHF, RCUT, and CVAL) of the Laboratoire de Physique Quantique of Toulouse. Table 2 presents a comparison between our calculation and experimental values of infinite NaK$^+$ molecular dissociation limits (the sum of atomic Na and K energies). We notice a very good agreement between the experiential [45] and our theoretical values. Such accuracy will be transmitted to molecular energy. The largest difference between experimental and theoretical limit does not exceed 50 cm^{-1} found for K(4*s*)–K(5*p*) atomic transition.

3. Potential energy curves and spectroscopic constants

The NaK$^+$ potential energy curves dissociating into Na(3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*) + K$^+$ and Na$^+$ + K(4*s*, 4*p*, 5*s*, 3*d*, 5*p*, 4*d*, 6*s*) have been computed for 300 distances *R*, that varies from 4 to 200 a.u. The $^2\Sigma^+$ electronic states are displayed in Fig. 1 and the remaining $^2\Pi$ and $^2\Delta$ states are displayed in Fig. 2. The spectroscopic constants of the ground and the six first excited states are presented in Tables 3A and 3B and compared with the available works [16–21]. Table 4 is devoted only to our spectroscopic
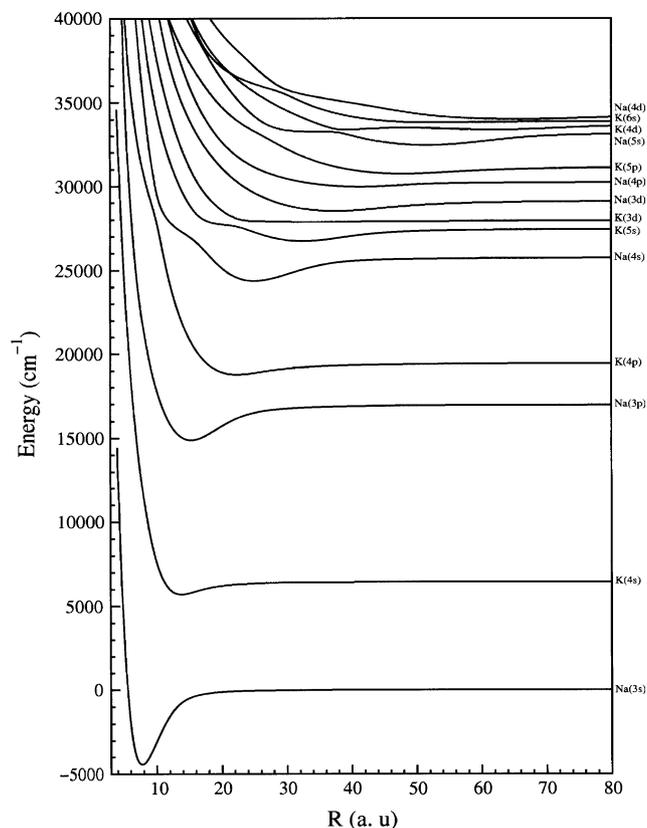
constants for the higher excited states studied here for the first time. Theoretically, the ground state was extensively studied. We found for this state the following spectroscopic constants $R_e = 7.75$ a.u., $D_e = 4442$ cm^{-1}, $\omega_e = 91.00$ cm^{-1}, $\omega_e \chi_e = 0.36$ cm^{-1}, and $B_e = 0.069212$ cm^{-1}. These values are in general agreement with all other theoretical values (see Tables 3A and 3B), knowing that our equilibrium distance R_e is overestimated and our D_e is underestimated. In particular, there is a good agreement between our work and that of Müller and Meyer [17] ($R_e = 7.71$ a.u., $D_e = 4581$ cm^{-1}, $\omega_e = 91.90$ cm^{-1}) and as well as with the study of Magnier and Millié [16] ($R_e = 7.65$ a.u., $D_e = 4645$ cm^{-1}, $\omega_e = 91.00$ cm^{-1}). Such agreement is not surprising since we used similar methods. The only difference between our work and that of Müller et al. is the large basis set and the *l*-dependent cutoff radius that are used in our study. However, they used a small basis set and an average cutoff radius for all (*s*, *p*, *d*, and *f*) orbitals. Magnier and Millié [16] have reported in their paper only R_e, D_e, and ω_e of the NaK$^+$ ground state as their work has been devoted essentially to the NaK neutral molecule.

For the first six excited states, we compare our results with only the theoretical work of Valence et al. [21]. They reported, for the 2 $^2\Sigma^+$ state, the spectroscopic constants $R_e = 13$ a.u. and $D_e = 1390$ cm^{-1} to be compared with
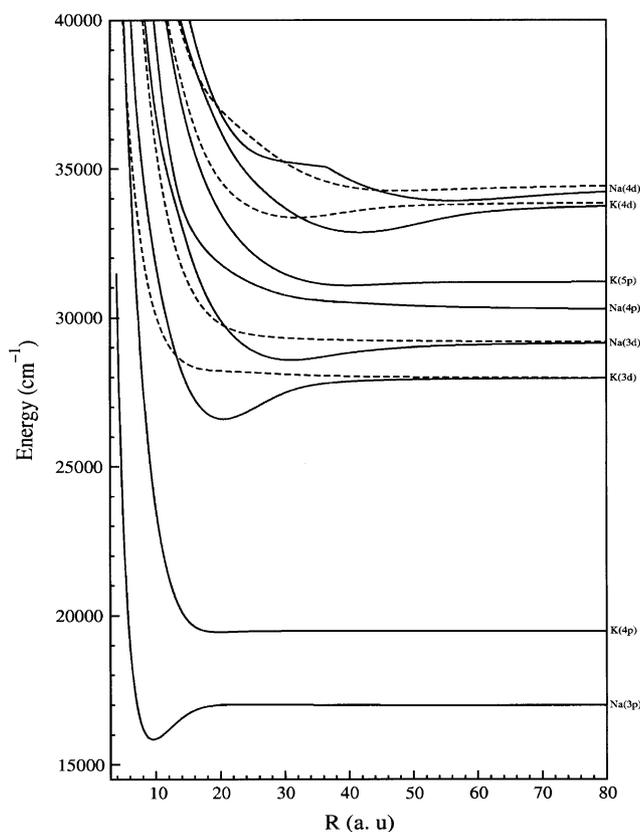
Fig. 2. Potential energy curves for the $^2\Pi$ (solid lines) and $^2\Delta$ (dashed lines) lowest electronic states of NaK$^+$ dissociating into Na(3p, 3d, 4p, 4d) + K$^+$ and Na$^+$ + K(4p, 3d, 5p, 4d).

our values of, respectively, $R_e = 13.81$ a.u. and $D_e = 742$ cm^{-1}. A rather good agreement is observed for the equilibrium distance, however, their potential is much deeper. For the 3 $^2\Sigma^+$ and 1 $^2\Pi$ states, Valance et al. [21]

have reported in their paper that these states exhibit small potential wells but they did not give their spectroscopic constants. From their Table 5, we can observe that these states have minimums around 15 and 11 a.u., which are rather close to our equilibrium distances of, respectively, 15.37 and 9.58 a.u. In contrast, in our work both states present significant well depths of, respectively, 2080 and 1119 cm^{-1}. The 4 $^2\Sigma^+$, 2 $^2\Pi$, and 5 $^2\Sigma^+$ states were found in the work of Valance et al. [21] to be repulsive, while in our study they are attractive. The 2 $^2\Pi$ state exhibits a very small van der Waals well of 20 cm^{-1} located at 19.92 a.u. However, the 4 $^2\Sigma^+$ and 5 $^2\Sigma^+$ states are much more attractive. They present well depths of, respectively, 682 and 1371 cm^{-1} located at, respectively, 22.40 and 25.08 a.u. It is important to note that Valance et al. [21] 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.

The spectroscopic constants of the $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ higher excited states are presented here for the first time. Equilibrium distance of all these states is found for intermediate and large values of internuclear distance. All of the 6–14 $^2\Sigma^+$ excited states are attractive with potential well depths of some 100 cm^{-1} except the 13 $^2\Sigma^+$ state, which has a well depth $D_e = 71$ cm^{-1} located at large internuclear equilibrium distance $R_e = 52.68$ a.u. The 12 $^2\Sigma^+$ state exhibits a double well of closed depths of, respectively, 476 and 482 cm^{-1} located at large internuclear distance of, respectively, 39.08 and 62.20 a.u. The existence of the 12 $^2\Sigma^+$ double well is due to the avoided crossing between this state and the 13 $^2\Sigma^+$ state. The 3 $^2\Pi$ and 7 $^2\Pi$ states have rather large well depths of, respectively, 1377 and 1000 cm^{-1} at, respectively, 20.50 and 41.71 a.u., while the 4, 6–8 $^2\Pi$ states have potential wells of hundred of cm^{-1}. The 5 $^2\Pi$ state is

Table 3A
Spectroscopic constants for the first six $^2\Sigma^+$ and $^2\Pi^+$ electronic states of NaK$^+$ molecule

State	R_e (a.u.)	D_e (cm^{-1})	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})	Reference
1 $^2\Sigma^+$	7.75	4442		91.00	0.36	0.069212	This work
	7.65	4645		91.00			[16]
	7.71	4581		91.90			[17]
		4645					[18]
	7.67	4614					[19]
	7.67	4670					[20]
	7.2	5138					[21]
	7.6	4678					[21]
2 $^2\Sigma^+$	13.81	742	10142	32.63	0.32	0.021806	This work
	13.00	1390					[21]
3 $^2\Sigma^+$	15.37	2080	19330	34.01	0.08	0.017609	This work
1 $^2\Pi$	9.58	1119	20292	39.92	0.44	0.045295	This work
4 $^2\Sigma^+$	22.40	682	23226	17.77	0.89	0.008295	This work
		Repulsive					[21]
2 $^2\Pi$	19.92	20	23887	8.78	0.51	0.010473	This work
		Repulsive					[21]
5 $^2\Sigma^+$	25.08	1371	28827	19.76	0.10	0.006612	This work
		Repulsive					[21]

Table 3B
Spectroscopic constants for the higher excited $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ electronic states of NaK$^+$ molecule

State	R_e (a.u.)	D_e (cm^{-1})	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})
6 $^2\Sigma^+$	32.68	728	31174	12.48	0.03	0.003893
7 $^2\Sigma^+$	36.37	102	32318	2.27	7.47	0.003209
3 $^2\Pi$	20.50	1377	31043	20.76	0.14	0.009891
1 $^2\Delta$		Repulsive				
8 $^2\Sigma^+$	37.49	652	32966	8.90	0.28	0.002959
4 $^2\Pi$	31.06	598	33019	10.57	0.44	0.004313
2 $^2\Delta$		Repulsive				
9 $^2\Sigma^+$	41.28	285	34431	7.28	0.03	0.002440
5 $^2\Pi$		Repulsive				
10 $^2\Sigma^+$	47.89	445	35189	7.18	0.05	0.001813
6 $^2\Pi$	39.83	109	35526	6.16	0.09	0.002622
11 $^2\Sigma^+$	51.52	758	36899	8.17	0.01	0.001567
12 $^2\Sigma^+$	39.08	476	37825	13.96	0.56	0.002724
	62.20	482	37819	4.73	0.56	0.002724
7 $^2\Pi$	41.71	1000	37301	8.98	0.05	0.002391
3 $^2\Delta$	32.05	491	37810	9.19	0.08	0.004049
13 $^2\Sigma^+$	52.68	71	38265	3.41	0.11	0.001498
14 $^2\Sigma^+$	65.40	548	38458	4.09	0.01	0.000972
8 $^2\Pi$	56.31	636	38371	5.80	0.01	0.001312
4 $^2\Delta$	47.65	292	38713	4.71	0.05	0.001832

Table 4
R_c (a.u.): the avoided crossing distances for ionic molecule NaK$^+$

States	R_c positions (a.u.)
3 $^2\Sigma$/4 $^2\Sigma$	4.470
4 $^2\Sigma$/5 $^2\Sigma$	10.115
6 $^2\Sigma$/7 $^2\Sigma$	22.700
8 $^2\Sigma$/9 $^2\Sigma$	8.750
9 $^2\Sigma$/10 $^2\Sigma$	7.495
	11.600
11 $^2\Sigma$/12 $^2\Sigma$	17.110
	37.860
12 $^2\Sigma$/13 $^2\Sigma$	14.900
	21.270
	49.970
13 $^2\Sigma$/14 $^2\Sigma$	8.000
	29.755
	64.945
4 $^2\Pi$/5 $^2\Pi$	13.840
8 $^2\Pi$/9 $^2\Pi$	12.750
	36.550

repulsive. We have also determined the potential energy curves of the first four states of $^2\Delta$ symmetry. The 1 $^2\Delta$ and 2 $^2\Delta$ states are repulsive, while the 3 $^2\Delta$ and 4 $^2\Delta$ states are attractive. They have minima at, respectively, 32.05 and 47.65 a.u. for well depths of, respectively, 491 and 292 cm^{-1}.

4. Avoided crossing

Many works on measuring the cross-section of the electron transfer between Li and Na in the LiNa$^+$ [46–49] ionic molecule were realized in the past. Another work [12] using the avoided crossing between the 4 $^2\Sigma$ and 5 $^2\Sigma$ states of the LiNa$^+$ molecule has been done recently to study the non-adiabatic dynamics by two-color ATD experiment. To

the best of our knowledge, there are no similar works on NaK$^+$ molecule. For this aim, we have determined with accuracy the position of such avoided crossing for further use. Some curves present more than two positions of avoided crossing leading to undulating feature of some excited states. In Table 4, we present the avoided crossing between many states: 6/7, 7/8, 8/9, 9/10, 12/13, and 13/14 $^2\Sigma$ states and 3/4, 7/8, 8/9, and 9/10 $^2\Pi$ states dissociating into both systems Na + K$^+$ and Na$^+$ + K. Such avoided crossing is a result of a charge transfer between each two states and finally between Na and K atoms.

The data produced in this work can be used to perform a simulation of one- and two-color experiment in above threshold dissociation (ATD) by monitoring an avoided crossing with femtosecond spectroscopy. Such study has already been done for some similar systems as LiNa$^+$ [12], Na$_2^+$ [50], and Li$_2^+$ [13].

5. Transition dipole moments

In addition to the calculation of the potential energy curves of 26 electronic states of $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ symmetries, we have determined the adiabatic transition dipole moments. Here, we present the transition dipole moment from the ground state $X\,^2\Sigma^+$ dissociating into Na(3s) + K$^+$ and from first excited states 2–4 $^2\Sigma^+$, dissociating into Na$^+$ + K(4s), Na(3p) + K$^+$, and Na$^+$ + K(4p), to higher excited states of the same symmetry. Fig. 3 corresponds to the transition dipole moment from $X\,^2\Sigma^+$ to other states. We remark that the most significant transition dipole moment is related to the transition between $X\,^2\Sigma^+$ and 2 $^2\Sigma^+$ states, which has a maximum of 3.48 a.u. located at 11.25 a.u. At this distance the two states present also a maximum overlap between their molecular orbitals. We expect that the photoabsorption spectrum will present a
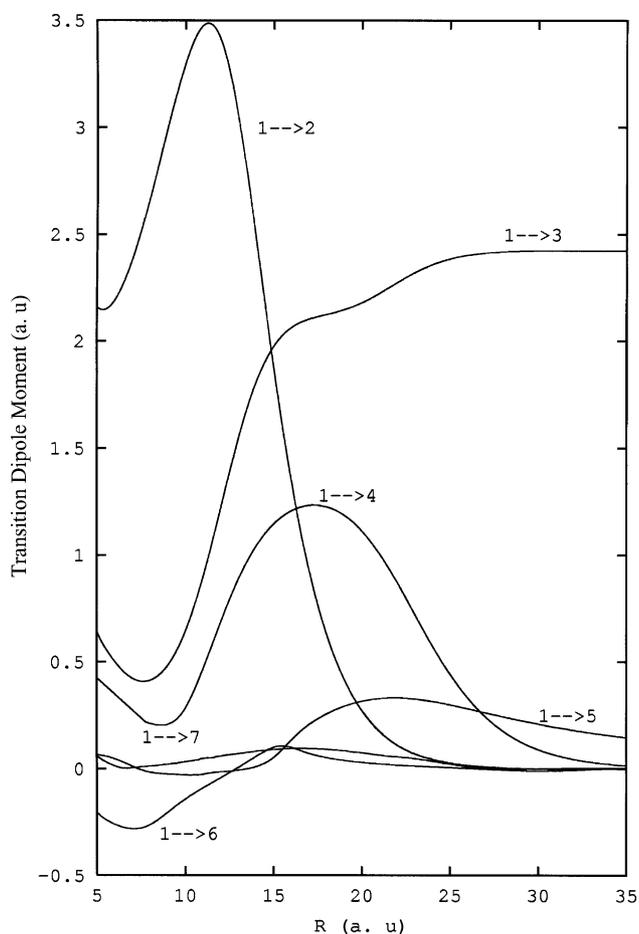
Fig. 3. Transition dipole moment from $X\ ^2\Sigma$ to the higher $^2\Sigma$ excited states.

Fig. 4. Transition dipole moment from $2\ ^2\Sigma$ to the higher $^2\Sigma$ excited states.

peak around this distance. At infinite distance, the transition dipole moment vanishes as the electron in the first state is on the Na atom and in the second state on K atom corresponding to an electron transfer. It corresponds to a pure atomic transition dipole moment between two different species Na(3s) and K(5s). The $X\ ^2\Sigma^+$–$3\ ^2\Sigma^+$ transition dipole moment starts from small values then it increases rapidly between 9.5 and 15.5 a.u. and finally it becomes a constant equal to 2.42 a.u., corresponding exactly to the atomic transition dipole moment between Na(3s) and Na(3p) to be compared with the experimental value of 2.377 a.u. The $X\ ^2\Sigma^+$–$4\ ^2\Sigma^+$ transition presents a maximum of 1.23 a.u. at 17.25 a.u. then it goes rapidly to zero corresponding to a forbidden transition between Na(3s) and K(4p). The X–$5\ ^2\Sigma^+$ transition tends to the atomic transition constant of 0.00668 a.u. The transition from $X\ ^2\Sigma^+$ to higher excited states is less important. It goes to zero if the atomic transtion is forbidden (from Na to K atoms or the inverse) and to a constant if the transtion is allowed. At very large distance, such transition corresponds to exactly the pure atomic one. In the same time, we have drawn in Fig. 4 the transition dipole moment between the $2\ ^2\Sigma^+$ state dissociating into Na$^+$ + K(4s) and the higher excited states. In general, we get the same behavior as we
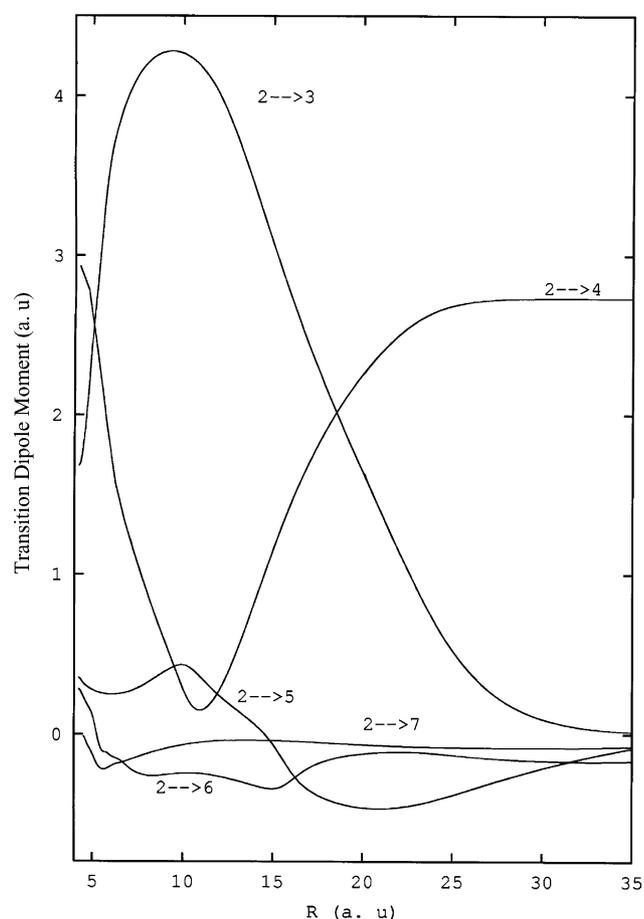
have got in Fig. 3 for the transition between the $X\ ^2\Sigma^+$ state and higher excited states. The largest transition is from $2\ ^2\Sigma^+$ to $3\ ^2\Sigma^+$ states dissociating into two different molecular systems Na$^+$ + K(5s) and Na(3p) + K$^+$. It has a maximum of 4.28 a.u. around 9.4 a.u. 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 K(5s)–K(5p), is a constant (2.725 a.u.). The higher transitions are less significant.

Fig. 5 presents the transition dipole moment from the $3\ ^2\Sigma^+$ state to more excited states. We remark that the 3–$4\ ^2\Sigma^+$ transition is very large. It presents a maximum of 7.18 a.u. located at 19.5 a.u. So it is expected that around this distance there is an important overlap between the corresponding wavefunctions. At large distance, the 3–$4\ ^2\Sigma^+$ transition dipole moment is much less important. It vanishes at infinite distance as it will correspond to a pure atomic transition between two different atoms Na(3p) and K(4p). The 3–$5\ ^2\Sigma^+$ transition dipole moment is still significant with a peak of 3.22 a.u. at 8.25 a.u. and a constant of 2.50 a.u. at infinite distance, corresponding to the atomic transition dipole moment between Na(3p) and Na(4s).

Fig. 6 presents the transition dipole moment between the $4\ ^2\Sigma^+$ state and the higher $^2\Sigma^+$ states. The 4–$5\ ^2\Sigma^+$ and 4–6
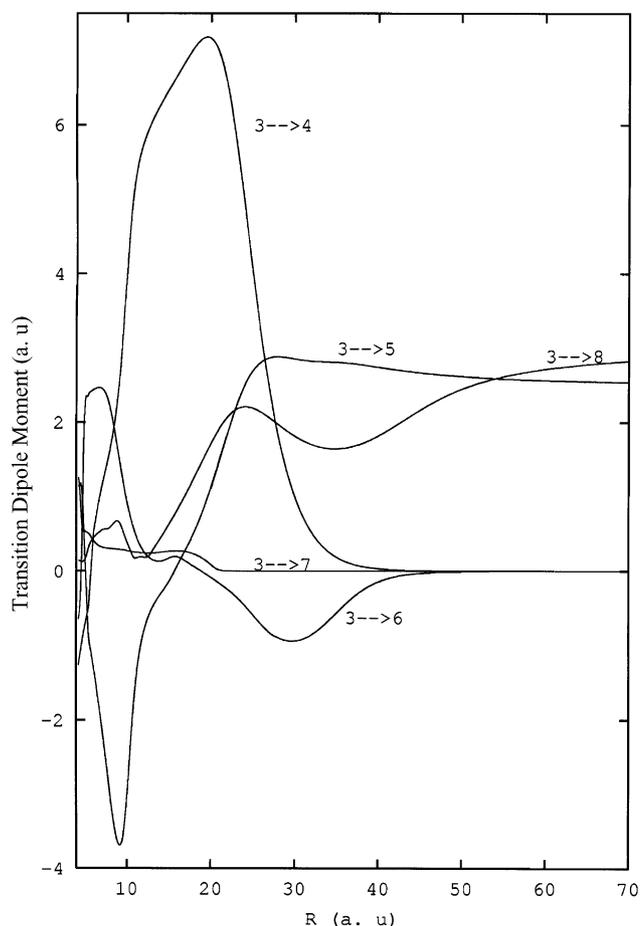
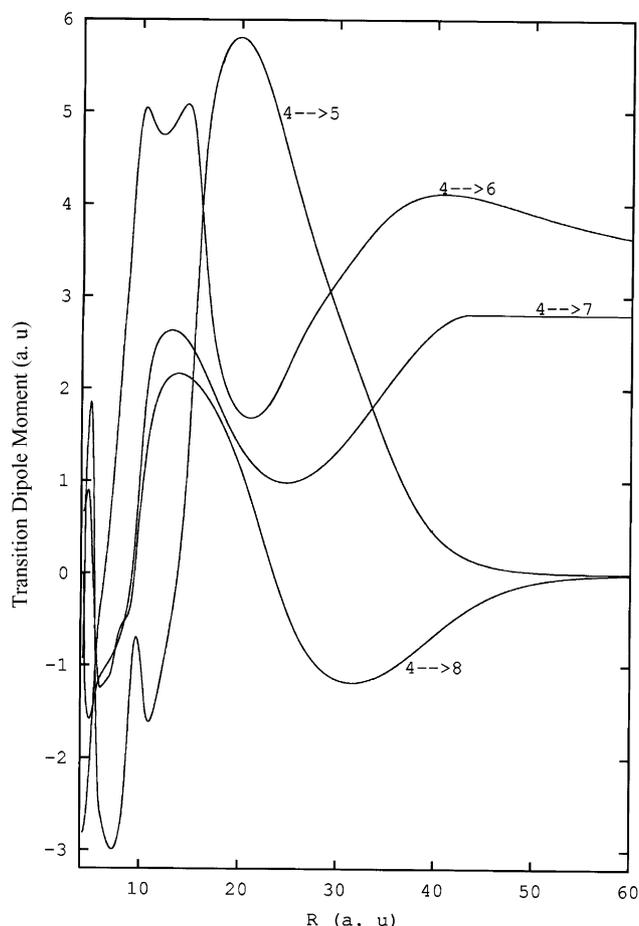Fig. 5. Transition dipole moment from 3 $^2\Sigma$ to the higher $^2\Sigma$ excited states.

Fig. 6. Transition dipole moment from 4 $^2\Sigma$ to the higher $^2\Sigma$ excited states.

$^2\Sigma^+$ transitions are the most significant ones. They present large values of, respectively, 5.80 and 5.08 a.u., located around, respectively, 20 and 14.5 a.u. At infinite distance, while the 4–5 $^2\Sigma^+$ transition tend to zero corresponding to forbidden atomic transition K(4p)–Na(4s), the 4–6 $^2\Sigma^+$ transition tend to a constant of 3.26 a.u. corresponding to a pure atomic transition K(4p)–K(4s). The 4–7 $^2\Sigma^+$ and 4–8 $^2\Sigma^+$ transitions are also rather large. They have maxima around 13 a.u. of values, respectively, 2.63 and 2.64 a.u. At infinite distance, the 4–8 $^2\Sigma^+$ transition vanishes and the 4–7 $^2\Sigma^+$ is a constant (2.80 a.u.) associated to the K(4p)–K(3d) atomic transition.

6. Conclusion

Using the pseudopotential approach for Na and K atoms, the NaK$^+$ ionic molecule was treated as a one-electron system where 26 potential energy curves dissociating up to Na(4d) + K$^+$ and Na$^+$ + K(6s) were computed with a good accuracy. A very good agreement for the ground state between our spectroscopic constants and those of the available references is observed. The first six excited states were compared with the work of Valance et al. [21]. The higher excited states are studied here for the first

time. For a best understanding of the potential energy curves' behavior and the electron charge transfer, we determined the avoided crossing positions between all the electronic states and we calculated the transition dipole moments from the ground and the three first excited states 2–4 $^2\Sigma^+$ to higher excited states. Several theoretical works have been done on NaK$^+$ but the majority was focused on the ground state. The study of Valence et al. [21] was the only theoretical work interested on the first excited states of NaK$^+$. In their work, the potential has been calculated for a maximum R limit of 20 a.u. It is a short distance to investigate the excited states having potential wells located at intermediate and large internuclear distances. Due to this, a discrepancy is observed between our and their works for the 4 $^2\Sigma^+$, 2 $^2\Pi$, and 5 $^2\Sigma^+$ states. To the best of our knowledge, no experimental study has been done until now on such ionic molecular system. In contrast, the neutral molecule NaK has been explored by theory and experience. Despite the absence of references for comparison of the presented results, we expect to reach a similar accuracy to many previous works that have used the same techniques.

For a better understanding of the charge transfer process between the two alkali Na and K atoms, a spin–orbit

coupling calculation for the potential energy curves will be carried out. It is expected that the avoided crossing positions will be slightly shifted. This work is actually on progress for several ionic alkali molecules.

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