Theoretical study of the electronic states and transition dipole moments of the LiK$^+$ molecule

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Abstract

The adiabatic potential energy, the spectroscopic constants and the transition dipole moments of the lowest electronic states of the LiK$^+$ molecule, dissociating into Li(2s, 2p, 3s, 3p, 3d, 4s, and 4p) + K$^+$ and Li$^+$ + K(4s, 4p, 5s, 3d, 5p, 4d, and 6s), have been investigated. We have used an ab initio approach involving a non-empirical pseudopotential for the Li $(1s^2)$ and K $(1s^22s^22p^63s^23p^6)$ cores and core valence correlation correction. A very good agreement has been obtained for the ground state for the spectroscopic constants with the available theoretical works. The transition dipole moment from X$^2\Sigma$, $2^2\Sigma$, $3^2\Sigma$, and $4^2\Sigma$ states to higher excited states have been determined. Numerous avoided crossing 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 Li$^+$K and LiK$^+$.
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Keywords: Ab initio; LiK$^+$ molecule; Transition dipole moment

1. Introduction

Diatomic molecules and their cations composed by hydrogen and alkali atoms 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. Homonuclear diatomic alkali molecules present probably the most understood diatomic molecules. Experimentally, they are relatively easy to be handled. Their spectroscopy has been extensively studied using high-resolution methods [1]. Theoretically, their reduced number of valence electrons allowed high quality of ab initio calculations [2]. Alkali and hydrogen alkali dimers form prototype systems for investigation of non-adiabatic coupling [3–5], collision process radiative association and dissociation [6–8], diabatisation and predissociation [5,9]. In theory,

several techniques have been used to study alkali dimers. Most of them have proposed to reduce the number of electrons to only valence electrons, by using pseudopotentials or model potential replacing the effect of core electrons on the valence electron. Both methods, a non-empirical pseudopotential techniques and model potential have been used in the past. In the model potential calculation—which has been developed by Bottcher and Dalgarno [10]—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 Li and K cores reduce the number of active electrons to only one valence electron, where the SCF calculation produces the exact energy in the basis 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. [11]. This formalism was used first for Rb$_2$ and RbCs molecules and later for several systems (LiH, LiH$^+$, Li$_2^+$,

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and LiNa$^+$) and its use has demonstrated efficiency. The non-empirical pseudopotentials permit the use of very large basis sets for the valence and Rydberg states and allow accurate descriptions for the highest excited states.

Despite the relative simplicity of the LiK$^+$ system, few theoretical works have been done and, for our best knowledge, there are no experimental study done till now. The neutral molecule LiK was explored by many theoretical [12,13] and experimental [14,15] works. The only theoretical works existing on LiK$^+$ are the work of Müller et al. [12] and that of von Szentplay [16] where only the ground state has been studied. In the work of Müller et al. the aim was to test the pseudopotential formalism at the SCF level for diatomic molecules having two and one valence electrons. Information on heteronuclear ionic alkali diatomic molecules is quite scarce. For experimentalists, the formation of AB$^+$ systems (A and B are alkali atoms) is dominated by the formation of A$_2^+$ and B$_2^+$ due to the difference of the melting points to produce A and B in vapour form. For theoretists, the absence of experimental data has limited their interest in studying the neutral and ionic heteronuclear alkali dimers. This paper presents for the first time the excited electronic states of the LiK$^+$ molecule. In this study LiK$^+$, having only one active electron, will be a one of the simplest heteromolecular systems and the computing time is reduced. The present work succeeds our study on many diatomic systems, such as LiH [5], LiH$^+$ [17], and LiNa$^+$ [18] and triatomic systems such as LiH$_2$ [19,20] where we used the same techniques. For all of them we got a remarkable accuracy showing the validity of this approach. The present results for LiK$^+$ can be expected to reach a similar accuracy since the main restriction in the accuracy of the calculation is the basis set limitation only. We present a complete set of results including all Rydberg states.

In the Section 2 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 Li(2s, 2p, 3s, 3p, 3d, 4s, and 4p) + K$^+$ and Li$^+$ + K(4s, 4p, 5s, 5p, 4d, and 6s). In Section 4 we present the transition dipole moments from the ground and the first excited state to higher excited states. Finally we summarize our conclusion in Section 5.

2. Method of calculation

In this work, the Li and Na atoms are treated through a one electron non-empirical pseudopotential proposed by Barthelat et al. [21] and used in many previous works [5,17–20]. In addition we account for the core valence correlation by the use of the operatorial formulation of Müller et al. [22]. Following the Foucroult et al. [11] formalism, l-adjustable cut off has been

Table 1
l-dependent cutoff radii (in Bohr) for Li and K atoms

l	Li	K
s	1.434	2.067
p	0.982	1.905
d	0.600	1.96
f	0.400	1.96

Table 2
Asymptotic energy of the LiK$^+$ electronic states

Asymptotic molecular state	This work (cm^{-1})	Experimental (cm^{-1})	ΔE (cm^{-1})
Li(2s) + K$^+$ (1$^2\Sigma$)	0.00	0.00	0.00
Li(2p) + K$^+$ (3$^2\Sigma$, 1$^2\Pi$)	14905.55	14903.66	1.89
Li(3s) + K$^+$ (5$^2\Sigma$)	27211.78	27206.12	5.66
Li(3p) + K$^+$ (8$^2\Sigma$, 3$^2\Pi$)	30925.95	30925.38	0.57
Li(3d) + K$^+$ (9$^2\Sigma$, 5$^2\Pi$, 2$^2\Delta$)	31290.72	31283.08	7.64
Li(4s) + K$^+$ (11$^2\Sigma$)	35017.62	35012.06	5.56
Li(4p) + K$^+$ (14$^2\Sigma$, 8$^2\Pi$)	36475.36	36469.55	5.81
K(4s) + Li$^+$ (2$^2\Sigma$)	0.00	0.00	0.00
K(4p) + Li$^+$ (4$^2\Sigma$, 2$^2\Pi$)	13022.96	12985.17	37.79
K(5s) + Li$^+$ (6$^2\Sigma$)	21017.98	21026.8	8.82
K(3d) + Li$^+$ (7$^2\Sigma$, 3$^2\Pi$, 1$^2\Delta$)	21535.51	21534.42	1.09
K(5p) + Li$^+$ (10$^2\Sigma$, 6$^2\Pi$)	24750.81	24701.44	49.37
K(4d) + Li$^+$ (12$^2\Sigma$, 7$^2\Pi$, 1$^2\Delta$)	27417.21	27397.01	20.2
K(6s) + Li$^+$ (13$^2\Sigma$)	27451.88	27450.65	1.23

optimised to reproduce the atomic ionisation energy for the lowest states of each symmetry. The cut-off radii for the lowest valence s, p, d, and f one-electron states are reported in Table 1.

For Li we used the same basis set of gaussian-type orbital (GTO's) as in our previous works [17–20]. For K atom we use the basis set of Magnier et al. [23] which was built at the first by Jeung and Ross [24] and developed by adding more diffuse orbital necessary for the description of highly excited states. The core dipole polarizability of Li and K are, respectively, 0.1915 and 5.354 a_0^3 (taken from [12]). Table 2 presents a comparison between our calculation and experimental values of ionization potential (IP) and atomic energy levels. As it seems there is a very good agreement between experimental [25] and our theoretical values. Such accuracy will be transmitted to molecular energy. The potential energy calculations have been performed using the standard chain of programs of the quantum physics laboratory of Toulouse.

3. Potential energy curves and spectroscopic constants

Potential energy curves have been computed for 25 molecular states dissociating into Li(2s, 3p, 3s, 3p, 3d, 4s, and 4p) + K$^+$ and Li$^+$ + K(4s, 4p, 5s, 3d, 5p, 4d, and 6s). They have been calculated for a large and dense grid of interatomic distances from 4 to 200 a.u. Table 2

presents a comparison between our theoretical dissociation limit and experimental ones. Our molecular dissociation values correspond to the calculated atomic energies levels for Li and K atoms. The difference between experimental and theoretical values does not exceed 50 cm^{-1}. Such excellent agreement between theoretical and experimental dissociation energies shows the high quality of the used basis sets. The accuracy of the atomic energy will be transmitted to molecular calculation. The spectroscopic constants (R_e, D_e, T_e, ω_e, $\omega_e\chi_e$, and B_e) of the ground and low lying states are presented in Tables 3 and 4 and compared with other theoretical works. For our best knowledge, the only theoretical works realized for LiK$^+$ are the work of Müller et al. [12] and that of von Szentpàly et al. [16] and there is no experimental work on such system. Table 3 corresponds to a comparison between the available theoretical works [12,16] and our study. Müller et al. report the spectroscopic constants for many neutral and ionic alkali dimers but only for the ground state.

Table 3
A comparison of the spectroscopic constants for the X$^2\Sigma$ electronic state of LiK$^+$ with the available works

Reference	R_e (a.u.)	D_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})
This work	7.34	4663	152.12	1.45	0.1895661
[12]	7.32	4807	154.1	0.94	0.189
[16]	7.26	4847	156		0.194

Table 4
Spectroscopic constants for the excited $^2\Sigma$, $^2\Pi$, and $^2\Delta$ electronic states of LiK$^+$ 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})
$2^2\Sigma$	12.79	1038	12103	62.17	0.56	0.062448
$3^2\Sigma$	15.83	745	18824	39.74	0.34	0.040772
$1^2\Pi$	9.20	50	9419	49.16	2.98	0.119830
$4^2\Sigma$	18.99	1247	24916	38.89	0.89	0.028314
$2^2\Pi$	16.74	96	26067	20.76	14.64	0.036147
$5^2\Sigma$	24.25	1531	30344	33.89	0.13	0.017373
$6^2\Sigma$	31.11	948	33210	21.02	0.60	0.010557
$7^2\Sigma$	36.19	124	34552	9.95	23.27	0.007690
$3^2\Pi$	20.00	1664	33012	32.02	0.41	0.025523
$1^2\Delta$	Repulsive					
$8^2\Sigma$	38.45	733	34856	15.34	0.84	0.006905
$4^2\Pi$	32.19	657	34932	14.07	1.18	0.009873
$9^2\Sigma$	Repulsive					
$5^2\Pi$	Repulsive					
$2^2\Delta$	Repulsive					
$10^2\Sigma$	42.31	713	37179	16.02	0.26	0.005706
$6^2\Pi$	36.52	152	37740	10.13	2.32	0.007682
$11^2\Sigma$	49.44	666	39015	11.90	0.35	0.004179
$12^2\Sigma$	38.13	371	40187	14.77	18.83	0.006965
	59.0	562	39996	8.72	18.83	0.002926
$7^2\Pi$	39.53	766	39791	15.05	0.73	0.006535
$3^2\Delta$	30.85	272	40286	11.56	27.87	0.010572
$13^2\Sigma$	50.27	85	40508	7.51	0.76	0.004046
$14^2\Sigma$	70.86	26	41112	3.46	0.17	0.002034
$8^2\Pi$	Repulsive					

Our ground state equilibrium distance R_e is in very good agreement as well as the dissociation energy D_e with their work. We find for R_e and D_e, respectively, 7.34 a.u. and 4663 cm^{-1} and they found 7.32 a.u. and 4807 cm^{-1}. The difference between our and their values is 0.02 a.u. for R_e and 134 cm^{-1} for D_e. For D_e, the difference between our and their values is about 100 cm^{-1}, which corresponds as they said in their paper [12] to the accuracy of their calculation. This good agreement between our results and those of Müller et al. for the ground states is also observed for ω_e, $\omega_e\chi_e$, and B_e spectroscopic constants. Our values for ω_e, $\omega_e\chi_e$, and B_e, are, respectively, 152.12, 1.45, and 0.189561 cm^{-1} and their values are 154.1, 0.94, and 0.189 cm^{-1}. This good agreement for the spectroscopic constants for the ground state is not surprising since we used similar methods. The only difference between our and their works is the large basis set and the l-dependent cut-off radius used in our study since they used a small basis set and an average cut off radius for all (s, p, d, and f) orbitals. von Szentplay et al. [16] report for the ground state only R_e, D_e, ω_e, and B_e spectroscopic constants. They found for them, respectively, 7.26 a.u., 4847, 156, and 0.194 cm^{-1}. We remark also a good agreement between our and their values.

Spectroscopic constants for $^2\Sigma$ excited states are presented here for the first time. Equilibrium distance of all theses states is found for intermediate and large values of the internuclear distance, from 12.79 to 70.86 a.u. We remark that only the $9^2\Sigma$ state, which is dissociating into Li(3d) + K$^+$, is repulsive. The potential of the ground state is the deepest one in comparison with $^2\Sigma$ excited states or other symmetries. The well depth of the $14^2\Sigma$ is very small (26 cm^{-1}) corresponding to a very large intermolecular equilibrium distance of 70.86 a.u. Potential energy curves are drawn on Fig. 1 for $^2\Sigma$ states and Fig. 2 for $^2\Pi$ and $^2\Delta$ states. Fig. 1 shows the depth of the well of the ground state in comparison with the others. The potential wells of the 2, 4, and $5^2\Sigma$ states still important. They present a well depth of, respectively, 1038, 1247, and 1531 cm^{-1} at 12.79, 18.99, and 24.25 a.u. The $3^2\Sigma$ state has a well depth of 745 cm^{-1} located at 15.83 a.u. We note that on the contrary of cations composed from hydrogen and alkali atoms, where the well is small in comparison with neutral molecule, in our case the well depth of the ionic system and that of the neutral system are of the same order (4663 and 5000 cm^{-1}). In our previous paper [18] on LiNa$^+$, we remarked that the ionic system is more bound than the neutral LiNa molecule. The difference between the two potential wells is about few hundreds of cm^{-1}. The higher excited states 5–14$^2\Sigma$, in contrast to the first five states, are very close to each other. They present many avoided crossings, which influence their behaviour. All of them present potential wells of some hundreds of cm^{-1} except the 13 and 14$^2\Sigma$ states, which are weakly

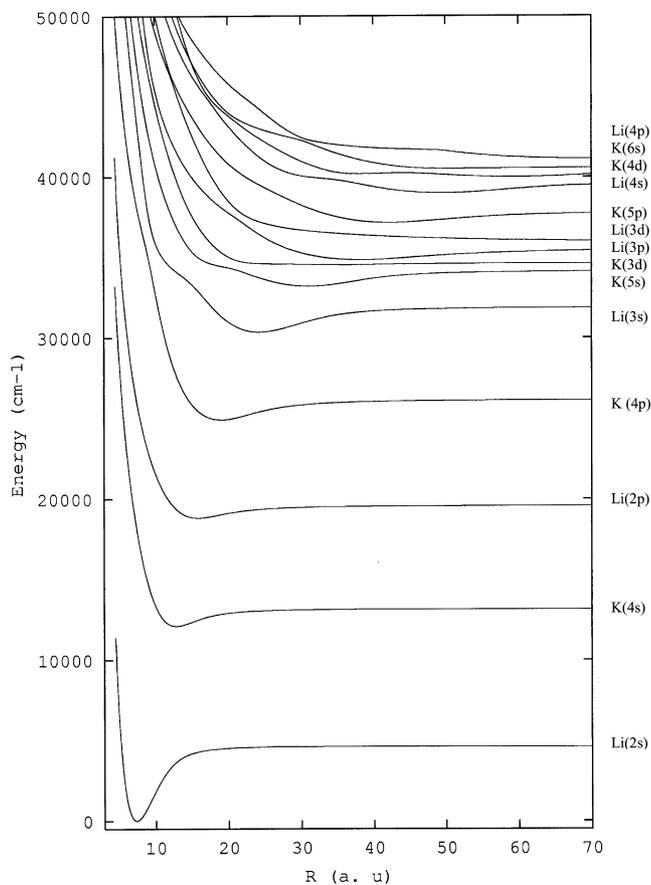Fig. 1. Potential energy curves for the lowest 1–14$^2\Sigma$ electronic states of LiK$^+$ dissociating into Li(2s, 2p, 3s, 3p, 3d, 4s, and 4p) + K$^+$ and Li$^+$ + K (4s, 4p, 5s, 3d, 5p, 4d, and 6s).
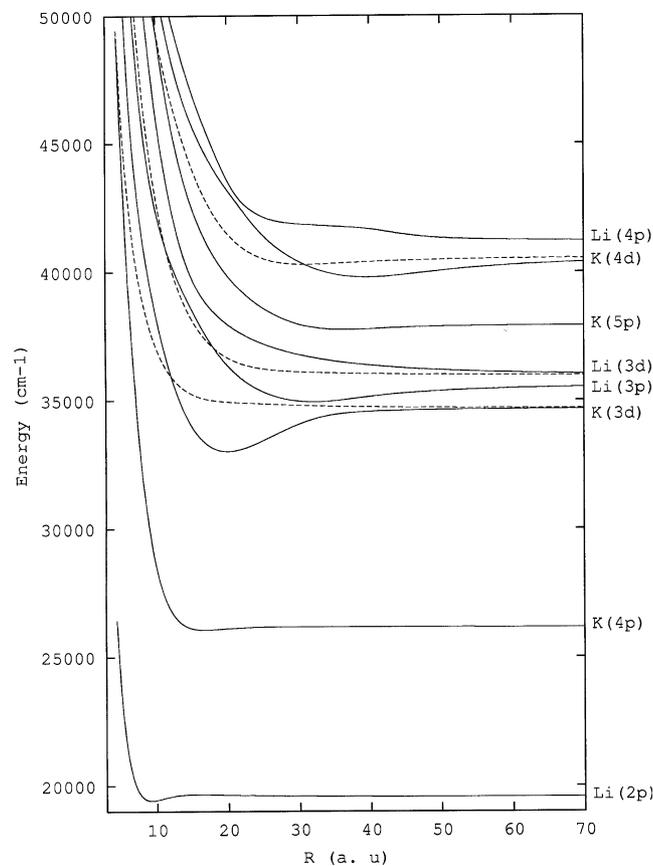

Fig. 2. Potential energy curves for the $^2\Pi$ (solid lines) and the $^2\Delta$ (dashed lines) lowest electronic states of LiK$^+$ dissociating into Li(2p, 3p, 3d, and 4p) + K$^+$ and Li$^+$ + K(4p, 3d, 5p, and 4d).

bound states with $D_e = 85$ and $26\ cm^{-1}$ at very large distances $R_e = 50.27$ and 70.86 a.u. The 6, 8, 10, and 11 states have potential wells of some hundreds of cm^{-1} at large distances. Their D_e are, respectively, 948, 733, 713, and $666\ cm^{-1}$ and their equilibrium positions (R_e) are, respectively, 31.11, 38.45, 42.31, and 49.44 a.u. The 12$^2\Sigma$ state has a particular shape. It has a double well of, respectively, 371 and $562\ cm^{-1}$ at 38.13 and 59.08 a.u. The barrier between the two wells is located at a position $R = 44.2$ a.u. for an energy of $40\,236\ cm^{-1}$. The first well is due to avoided crossing between 11$^2\Sigma$ and 12$^2\Sigma$ states and the second one is due the avoided crossing between 12$^2\Sigma$ and 13$^2\Sigma$ states. Knowing that 11$^2\Sigma$, 12$^2\Sigma$, and 13$^2\Sigma$ states dissociated into Li(4s) + K$^+$, Li$^+$ + K(4d), and Li$^+$ + K(6s); we can say that the first crossing is due to a charge transfer between Li and K. If we do not consider the 12$^2\Sigma$ state, which have a double well, the equilibrium distance of the $^2\Sigma$ states is increasing from 7.34 to 70.86 a.u. In fact most of the potential wells are due to the avoided crossings between neighbour states. Such avoided crossings are also related to charge transfer as for each couple of neighbour states the potential energy curves are dissociating into Li + K$^+$ and Li$^+$ + K or the inverse.

Fig. 2 shows the eight $^2\Pi$ and the three $^2\Delta$ lower excited states. The 1$^2\Pi$ state has a small well of a depth of $150\ cm^{-1}$ at intermediate distance of 9.23 a.u. Also the 2$^2\Pi$ state presents a small well of a depth of $96\ cm^{-1}$ at 16.74 a.u. The higher excited states present minimums at large distance increasing from 20.0 to 39.53 a.u. The deepest potential for the $^2\Pi$ and $^2\Delta$ states, belongs to the 3$^2\Pi$ state corresponding to a well depth of $1663\ cm^{-1}$ at 20.0 a.u. The 4, 6, and 7$^2\Pi$ states present well depths of hundreds of cm^{-1}, respectively, 657, 152, and $766\ cm^{-1}$ located, at relatively large distances, respectively, 32.19, 36.52, and 39.53 a.u. The 5$^2\Pi$ and 8$^2\Pi$ states are repulsive. For the $^2\Delta$ states we present 3 states dissociating into Li(3d) + K$^+$ and Li$^+$ + K(3d, 4d). The 1$^2\Delta$ and 2$^2\Delta$ states are repulsive although the 3$^2\Delta$ state is attractive. It presents a well of $275\ cm^{-1}$ located at $R_e = 30.77$ a.u.

In Table 5 we present the position R_c of avoided crossing between many states: 4/5, 6/7, 7/8, 8/9, 9/10, 11/12, 12/13, and 13/14$^2\Sigma$ states and 3/4, 7/8$^2\Pi$ states dissociating into both systems Li + K$^+$ and Li$^+$ + K. Most of the avoided crossings are due to the charge transfer between each two states and finally between Li and K atoms. Many works on measuring cross section of the electron transfer between Li and Na in the

Table 5
R_c (in a.u.): the avoided crossing distance positions

States	R_c position (a.u.)
$4^2\Sigma/5^2\Sigma$	9.29
$6^2\Sigma/7^2\Sigma$	20.96
$7^2/8^2\Sigma$	9.99
	39.13
$8^2\Sigma/9^2\Sigma$	7.60
	21.74
$9^2\Sigma/10^2$	6.80
	12.11
$11^2\Sigma/12^2\Sigma$	17.26
	35.25
$12^2\Sigma/13^2\Sigma$	9.240
	14.900
	20.010
	46.725
$13^2\Sigma/14^2\Sigma$	7.000
	13.100
	30.505
$3^2\Pi/4^2\Pi$	36.105
$7^2\Pi/8^2\Pi$	7.750
	21.255

LiNa$^+$ [26–29] ionic molecule was realised in the past. For our best knowledge there are no similar works on the LiK$^+$ molecule. Another work [30] using the avoided crossing between the 4 and $5^2\Sigma$ states of the LiNa$^+$ molecule was done recently to study the non-adiabatic dynamics by two-colour ATD experiment. 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 undulating feature of the potential of some excited states.

4. Transition dipole moments

To supplement this work on the LiK$^+$ molecule we determined the adiabatic transition dipole moments. Here we present the transition dipole moment from 1 to $4^2\Sigma$ states dissociating, respectively, into Li(2s) + K$^+$, Li$^+$ + K(4s), Li(2p) + K$^+$, and Li$^+$ + K(4p) to higher excited states of the same symmetry. Fig. 3 corresponds to transition dipole moment from X$^2\Sigma$ to other states. We remark that the most important curve present the transition moment between X$^2\Sigma$ and $2^2\Sigma$ sates. At infinite distance the electron in the ground state is on the Li atom and in the first excited state on K atom. At distance separation R around 10 a.u, we remark an important transition dipole moment presenting also a maximum overlap between the two molecular orbitals. We expect that the photoabsorption spectrum will present a peak around this distance. At large distance the X$^2\Sigma$–$2^2\Sigma$ transition moment vanishes corresponding to a pure atomic transition dipole moment between two different species Li(2s) and K(4s). The X$^2\Sigma$–$3^2\Sigma$ transition dipole moment starts
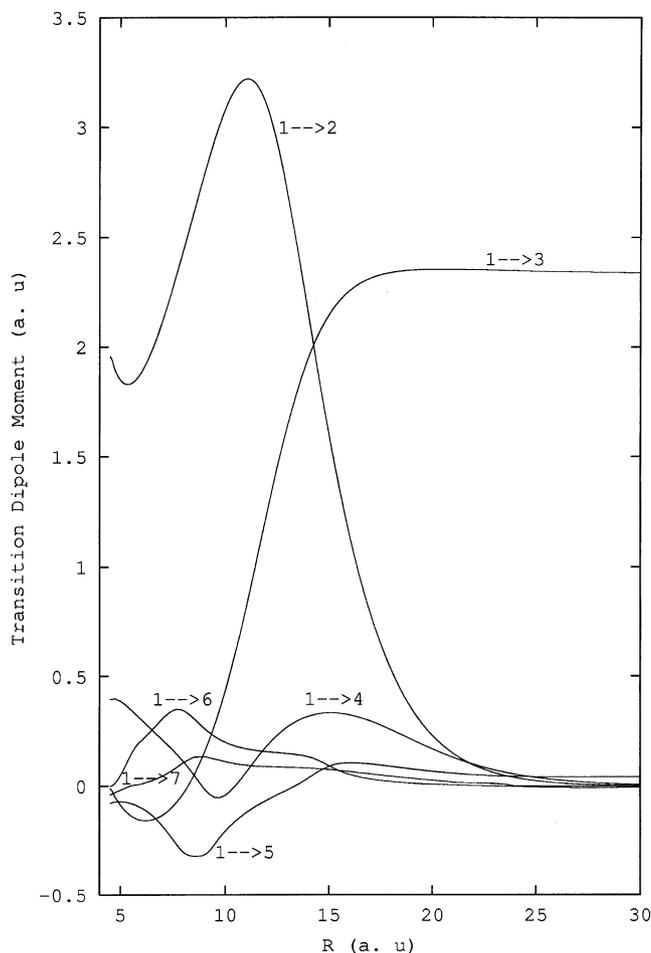

Fig. 3. Transition dipole moment from X$^2\Sigma$ to the higher $^2\Sigma$ excited states.

from small values then it increases rapidly between 10 and 15 a.u. and finally becomes a constant equal to 2.33 a.u., corresponding exactly to the transition dipole moment between Li(2s) and Li(2p) to be compared with the experimental value [31] of 2.35 a.u. The transition from X$^2\Sigma$ to higher excited states are less important. They go to zero when the atomic transition is forbidden (from Li to K) and to a constant when the transition is allowed and corresponding at very large distance to exactly the pure atomic transition. In the same time we have drawn on Fig. 4 the transition dipole moment between the $2^2\Sigma$ state dissociating into Li$^+$ + K(4s) and the higher excited states. We get the same behaviour as we have got in Fig. 3 for transitions between the X$^2\Sigma$ state and higher excited states. The most important transition is from $2^2\Sigma$ to $3^2\Sigma$ states dissociating into two different molecular systems Li$^+$ + K(4s) and Li(2p) + K$^+$. It has a maximum around 10 a.u., and 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 equal to 2.726 a.u. Fig. 5 presents the transition dipole moment from the $3^2\Sigma$ state dissociating into Li(2p) + K$^+$ to higher excited

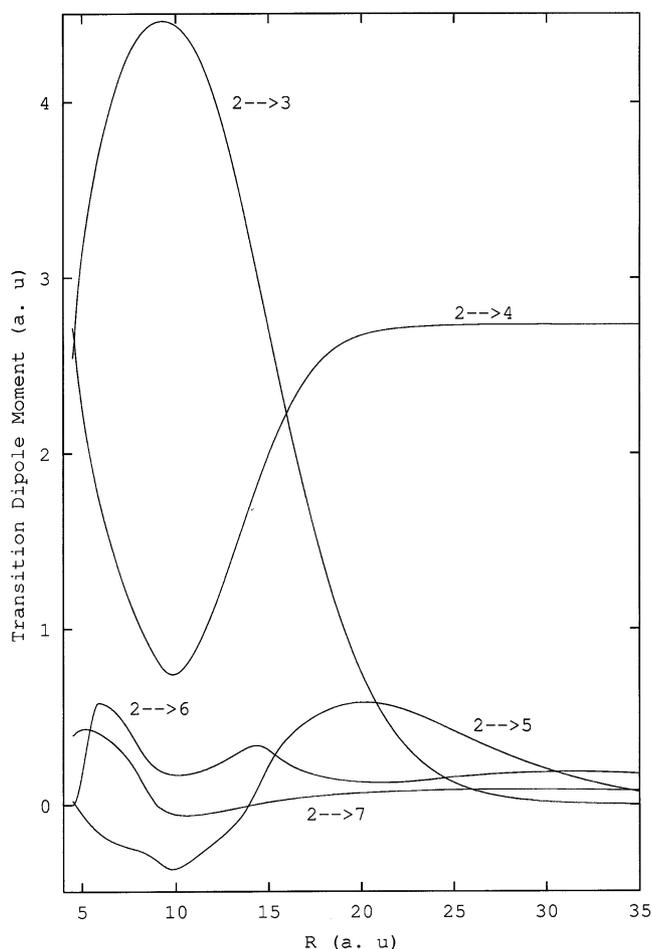Fig. 4. Transition dipole moment from $2^2\Sigma$ to the higher $^2\Sigma$ excited states.

Fig. 5. Transition dipole moment from $3^2\Sigma$ to the higher $^2\Sigma$ excited states.

states. The $3^2\Sigma$–$4^2\Sigma$ transition is the most important one. It has a maximum around 13 a.u. then it vanishes rapidly as at large distance it corresponds to a forbidden atomic transition between Li(2p) and K(4p). The $3^2\Sigma$–$5^2\Sigma$ transition is also important and presents a maximum around 9 a.u. then it decreases, in absolute value, to a constant equal to 1.657126 a.u. corresponding to the atomic transition between Li(2p) and Li(3s). The $3^2\Sigma$–$6^2\Sigma$ transition has a maximum around 8 a.u. and becomes zero at infinite distance as well as the $3^2\Sigma$–$7^2\Sigma$ transition. In contrast the $3^2\Sigma$–$8^2\Sigma$ transition, at infinite distance, is a constant of 0.206221 a.u. corresponding to the atomic transition between Li(2p) and Li(3p). In Fig. 6 we report the most important transition dipole moments between $4^2\Sigma$ state and the higher excited states. It seems that all of them present important dipole moment but the most important is between $4^2\Sigma$ and $5^2\Sigma$ states, which presents a large transition moment of 5 a.u. around an interatomic distance of 20 a.u. At large distances the transitions $4^2\Sigma$–$6^2\Sigma$ and $4^2\Sigma$–$7^2\Sigma$ become constants (3.261124 and 2.80391 a.u.) corresponding to the atomic transitions between K(4p)–K(5s) and K(4p)–K(3d). The transition dipole moments between $4^2\Sigma$–$5^2\Sigma$ and

$4^2\Sigma$–$8^2\Sigma$, at large distance, are equal to zero corresponding to the forbidden atomic transitions between K(4p)–Li(3s) and K(4p)–Li(3p).

5. Conclusion

Using the pseudopotential approach for Li and K atoms, the LiK$^+$ was considered as a one-electron system and 25 potential energy curves were computed with a good accuracy. The agreement between the spectroscopic constants obtained in our work and those of the available references for only the ground state is very good. The higher excited states are studied here for the first time and the presented data can help experimental investigation on the LiK$^+$ molecular ion. For best understanding of the potential curves behaviour and the electron charge transfer, we determined the avoided crossing positions between all the electronic states and we calculated the transition dipole moment from the ground and the first excited states $2^2\Sigma$, $3^2\Sigma$, and $4^2\Sigma$ to higher excited states. The calculated transition dipole moments are important and reach, at large distances, the pure atomic transitions.
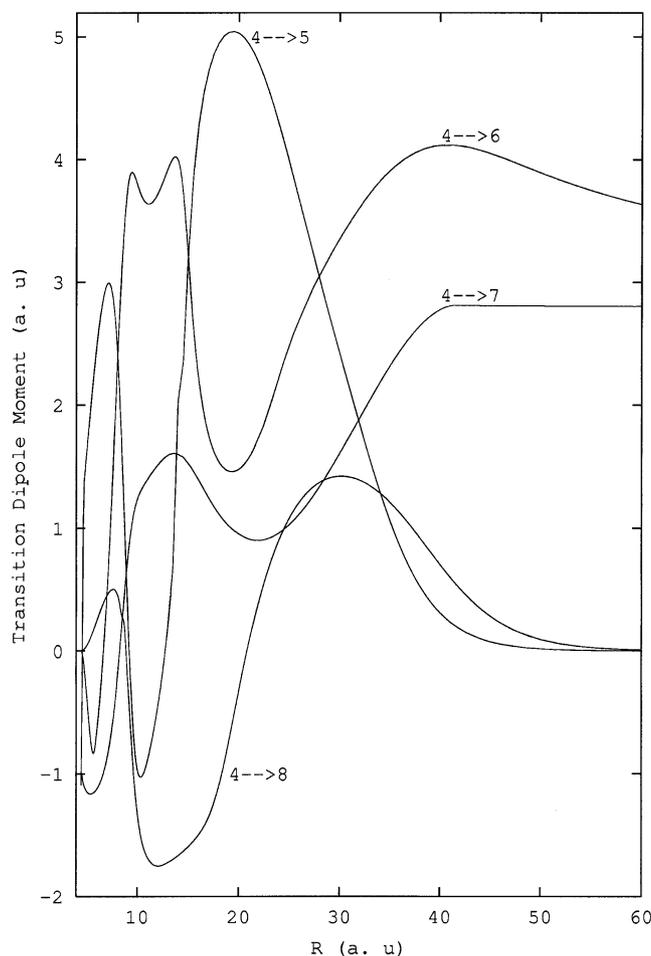
Fig. 6. Transition dipole moment from $4\,^2\Sigma$ to the higher $^2\Sigma$ excited states.

The data produced in this work can be used to perform a simulation of one and two-colour experiment in above threshold dissociation (ATD) by monitoring an avoided crossing with femtosecond spectroscopy. Such study was already done for some similar systems as LiNa$^+$ [29], Na$_2^+$ [32] and Li$_2^+$ [33]. Finally even on the relative simplicity of this system few theoretical works have been done and, for our best knowledge, there is no experimental study done until now on such ionic molecular system in contrast to the neutral molecule LiK, which was explored by theory and experience. Despite the absence of references for comparison for the presented results, we are expecting to reach a similar accuracy than many previous works using the same techniques, since the main restriction in the accuracy of the calculation is the basis set limitation only.

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