

A vibrational level spacing analysis of the LiK^+ lowest electronic states: Long-range behavior and evaluation of Li and K polarizabilities

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Abstract

A vibrational level spacing analysis of the lowest electronic states of the LiK^+ ionic molecule dissociating into $\text{Li}(2s, 2p, 3s, 3p, 3d, 4s \text{ and } 4p) + \text{K}^+$ and $\text{Li}^+ + \text{K}(4s, 4p, 5s, 3d, 5p, 4d, 6s)$ has been performed using the usual WKB semiclassical approximation. Accurate long-range potentials have been determined and allowing for the determination of all vibrational levels near the dissociation limit, the Li and K atomic polarizabilities, the number of trapped vibrational levels, and the vibrational turning points. The extracted polarizabilities for the ground levels of Li and K atoms have been compared with the available theoretical and experimental values. A very good agreement has been shown for them. The obtained atomic polarizabilities have been used to reproduce the long-range potential energy curves showing the good agreement between the ab initio calculated and the analytical potentials. A systematic generation of the missed Numerov vibrational levels and their turning points near the dissociation limit was done for all the LiK^+ electronic states.

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1. Introduction

The electric polarizability and multipole moments of atoms and molecules is associated with many important characteristics of electronic structure, ionization potential, long-range interpolation and non-linear optics phenomena. In particular the dipole polarizability is an important property in theoretical modeling and treatments of interatomic potentials, electron–atom scattering and collision-induced spectral shifts [1]. Many studies of the dipole polarizability [2–24] of the ground state of Li and K atoms were done.

In our previous work [25] we have determined the potential energy curves of 25 electronic states of the LiK^+ molecule dissociating into $\text{Li}(2s, 2p, 3s, 3p, 3d, 4s \text{ and } 4p) + \text{K}^+$ and $\text{Li}^+ + \text{K}(4s, 4p, 5s, 5p, 4d \text{ and } 6s)$. The use of the pseudopotentials technique [26] for Li and K cores has

reduced the number of active electrons to only one valence electron, where the SCF calculation has produced the exact energy in the basis set. In this context, the main source of errors corresponds to the basis-set limitations. Furthermore, we have corrected the energy by taking into account the core–core and core–electron correlation following the formalism of Foucault et al. [27]. 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. The comparison of the spectroscopic constants had shown a very good agreement between our values and the rare available theoretical and experimental studies on such system.

The LiK^+ ionic systems present an interesting long-range behavior dominated by charge–dipole interactions. In this study, we use the accuracy of the ab initio calculation of the potential energy at long-range distances, to perform a vibrational spacing analysis for the ground and numerous excited states of $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ symmetries. The paper is structured as follows. In Section 2, the numerical method

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is presented. Section 3 is devoted to present the extracted Li and K polarizabilities. In Section 4, we present the vibrational energy levels and we reproduce some potential energy curves using the long-range analytical form and the extracted polarizabilities. Finally we conclude.

2. Summary of the method

The LiK^+ ionic molecule was treated as a one-electron system. We have used the usual non-empirical pseudopotentials [26] in its semilocal form and we have taken into account the core valence correlation using the operational approach formalism of Müller et al. [14]. Following the formalism of Foucault et al. [27], l -adjustable cut off radii have been optimized to reproduce the atomic ionization energy for the lowest states of each symmetry. The used cut off radii and basis sets for Li and K atoms can be found in our previous work [25], which was focused on the adiabatic determination of the potential energy and transition dipole moments for 25 electronic states dissociating into $\text{Li}(2s, 2p, 3s, 3p, 3d, 4s, \text{ and } 4p) + \text{K}^+$ and $\text{Li}^+ + \text{K}(4s, 4p, 5s, 3d, 5p, 4d, \text{ and } 6s)$.

For the vibrational spacing analysis we have used the WKB semiclassical method. An excellent review of the WKB approximation applied to the vibrational diatomic molecules can be found in Ref. [28]. In this section we present briefly the used formalism to perform a long-range potential analysis.

The WKB semiclassical approximation, according to the development of Leroy and Bernstein [29], applied to a potential of the following expression:

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

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

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

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

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

In our case, at long-range distance, the potential energy behaves as a charge-dipole interaction and $n = 4$.

Using the last expression for vibrational energy levels, the $(E_v - D)^{1/4}$ can be written as following:

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

The plot of $(E_v - D)^{1/4}$ 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

$$E(v) = D - 11.817045(v_D - v)^4 C_4^{-1} \mu^{-2} \quad (5)$$

and

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

3. Polarizabilities

The LiK^+ potential energy curves (see Fig. 1), used in this work to realize a vibrational spacing analysis in order to evaluate the atomic polarizabilities, have been presented and commented in our previous paper [25]. Their molecular properties, except those of the ground state, were determined for the first time. There was a very good agreement between our equilibrium distance as well as the well depth, corresponding to the dissociation energy, and the results of the only available theoretical work of Müller et al. [14]. We found 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} . It is important to note that the binding energy of the ionic LiK^+ molecule was found [25] to be of the same order than that of the neutral system. In contrast to the ground state, the higher excited states had presented equilibrium distance located

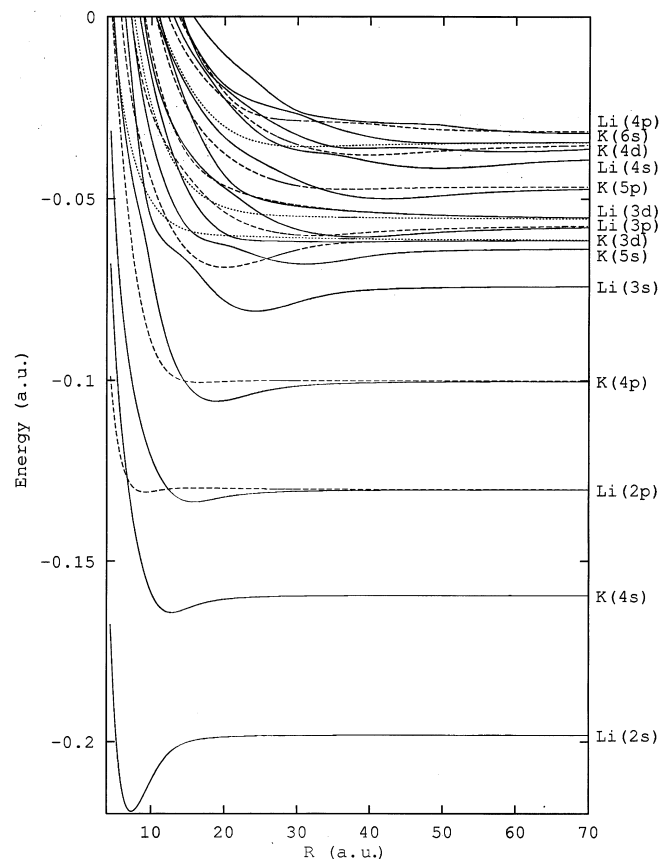


Fig. 1. Potential energy curves of 25 low lying electronic states of LiK^+ ionic molecule dissociating into $\text{Li}(2s, 2p, 3s, 3p, 3d, 4s, \text{ and } 4p) + \text{K}^+$ and $\text{Li}^+ + \text{K}(4s, 4p, 5s, 3d, 5p, 4d, \text{ and } 6s)$.

at intermediate and long-range distance. Their well depths were much smaller than that of the ground state. In addition to the electronic states study, we have determined and analyzed the transition dipole moments and the avoided crossings due to the charge transfer between LiK^+ and Li^+K ionic molecules.

Interestingly, the use of the semiclassical approximation give us additional information on the long-range potential through an analysis of the preliminary vibrational level progression and based on the remarkable adequacy of the linear fit of Eq. (4). According to the latter relation, a plot of $(E_v - D)^{1/4}$ versus v should be purely linear. Some plots are reported in Fig. 2 for 1–4, 6–7, 13–14 $2^2\Sigma^+$ states (bottom of Fig. 2) and 5, 8, 11–13 $2^2\Sigma^+$, 3–4, $7^2\Pi$ (top of Fig. 2). These plots are remarkably linear except for the last vibrational level of the $2^2\Sigma^+$ and $3^2\Pi$ states and the three last vibrational levels of the $13^2\Sigma^+$ state where a deviation from the linear fit is observed. This deviation can be explained by pure numerical problems in the determination of the vibrational energy levels by the Numerov algorithm as the energy difference between them becomes very small. In the asymptotic region serious difficulties may occur for the calculation of the vibrational energy levels near the dissociation limit. In this range of distance the vibrational wave function needs to be well described. That means that the ab initio potential has to be known in closed points and with a high accuracy. In deed, in this region the potential is known in sparse points with a limited accuracy (here 10^{-6} a.u.). The missed points in this region are determined in the Numerov algorithm by a cubic square. This will lead

to interpolation errors, which can become dramatic and give an oscillating potential. Therefore the deviation from the linear law for the last points in Fig. 2 can be taken as a measure of the numerical limitations previously mentioned.

In Table 1 we presented the different available experimental [2,6,7] and theoretical [3–5,8–24] polarizabilities of Li and K ground states. Most of them were taken from the recent work of Thakkar et al. [24] and that of Maroulis et al. [15]. As it seems from Table 1 a general agreement between the different works is observed for the Li atom. Our polarizability for the Li ground state (160.61 a.u.) is close to the experimental one (164 ± 3.4 a.u.) and in better agreement than the SCF [15], the uncoupled Hartree–Fock [3] and the coupled Hartree–Fock [4] calculations. They found, respectively, 169.1, 141.7, and 146.4 a.u. It is very important to note that our polarizability is directly extracted from the ground state potential using a vibrational spacing analysis based on the WKB semiclassical approximation. For the K ground state we find a polarizability of 289.2 a.u. to be compared with the experimental [6] value of 293 ± 6 a.u. Our value is in better agreement with the experience than the pseudopotentials [10] and the CI [14] values of, respectively, 298 and 287.1 a.u.

In addition to the ground states of Li and K atoms, we have reported in Table 2 the polarizabilities ($C_4 = \alpha/2$) for more ns excited levels such as 3s and 4s for Li and 5s for K. Such polarizabilities are compared with the available works [19,22,30–33]. Our static dipole polarizabilities for Li(3s) and K(5s) atoms are, respectively, 3812.1 and 4540.8 a.u.

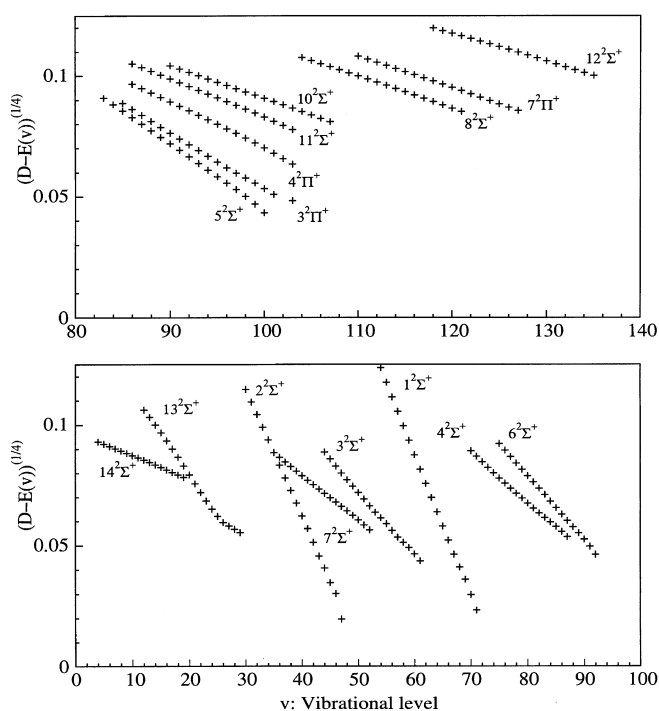


Fig. 2. Bottom: plot of $(E_v - D)^{1/4}$ versus v for 1–4, 6–7, 13, $14^2\Sigma^+$ electronic states of the LiK^+ molecule. Top: plot of $(E_v - D)^{1/4}$ versus v for 5, 8, 10–12 $2^2\Sigma^+$ and 3, 4, $7^2\Pi$ electronic states of the LiK^+ molecule.

Table 1

Comparison of our static dipole polarizabilities (in a.u.) of Li and K alkali atoms (in their ground states) with the available theoretical and experimental works

Year	Reference	Li	K
2005	This work	160.61	289.2
1963	[2]	148 ± 13	
1965	[3]	141.7	
1966	[4]	146.4	
1968	[5]	158.0	
1974	[6]	164.0 ± 3.4	396 ± 6
1974	[7]		305 ± 2
1976	[8]	170.3	
1979	[9]	170.1	298.0
1979	[10]	164.3	
1982	[11]	169.04	
1983	[12]	168.1	
1984	[13]	164 ± 2	287.1
1984	[14]	163.7	
1986	[15]	169.1	
1992	[16]	164.1	290
1993	[17]	164	
1994	[18]	164.19	
1995	[19]	161.71	
1996	[20]	164.11	
1999	[21]	163.74	302
2002	[22]	164	
2003	[23]	165.6	
2005	[24]	164.11	

Table 2

The static dipole polarizabilities of some excited atomic ns²S levels for Li and K atoms

	Li	v_D	K	v_D	References	
3s	3812.1	116.5	5s	4540.8	109.6	This work
	3825					[19]
	4098			4940		[22]
	4020					[30]
	4136					[31]
	4120					[32]
				4990		[33]
4s	34211.3	153.2				This work
	35040					[22]
	35260					[32]

They are in good agreement with the calculated values of Magnier et al. [22] given by, respectively, 4098 and 4940 a.u. We observe also the same good agreement between our polarizability (34211.3 a.u.) for the Li(4s) and that found by Magnier et al. (35,040 a.u.).

The calculation of the polarizabilities of some Li and K atomic levels dissociating into np and nd using $1/R^4$ long-range behavior has given large values in comparison with the available values of the recent work of Magnier et al. [22]. In contrast to the $^2\Sigma^+$ states dissociating to ns atomic limits the long-range behavior of the potential interaction is governed by both $1/R^3$ and $1/R^4$, corresponding to the interaction between the alkali ion charge and the atom quadrupole. In order to give more correct polarizabilities for such atomic levels, we have interpolated the potential energies of the electronic states dissociating into Li(np, nd) and K(np, nd) by the analytical form $\pm \frac{q}{R^3} - \frac{\alpha}{R^4}$ where q is the quadrupole moment and α is the parallel polarizability. The found values of α are displayed and compared with others works in Table 3. We report in Table 3, the static polarizabilities of the two lowest 2P excited levels of Li and K atoms determined by an analytical fit of our potential energy curves. A good agreement between our extracted values from the potential long-range behavior and the work of Magnier et al. [22] is observed.

Table 3

The static dipole polarizabilities for various atomic np_m ($m = \pm 1$) ²P of Li and K atoms

	Li	v_D	K	v_D	References	
2p ₀	127.8	77.7	4p ₀	419	113.6	This work
	128			509		[22]
	129					[30]
2p _{±1}	131.2		4p _{±1}	625.5		This work
	126			662		[22]
3p ₀	24041.5	101.25	5p ₀	6714	166.8	This work
	24621			6038		[22]
3p _{±1}	25373.8		5p _{±1}	7016.3		This work
	27645			7505		[22]

Table 4

Vibrational energy level spacing ($E_v - E_{v-1}$) (in cm⁻¹) of the LiK⁺ low lying states

v	1 ² Σ ⁺	2 ² Σ ⁺	3 ² Σ ⁺	4 ² Σ ⁺	5 ² Σ ⁺	6 ² Σ ⁺	7 ² Σ ⁺	8 ² Σ ⁺
0								
1	150.64	60.11	38.51	39.19	33.16	21.13	6.44	13.73
2	148.86	58.36	37.46	38.64	32.86	20.96	6.06	13.65
3	146.91	56.57	36.40	38.13	32.66	20.86	5.68	13.63
4	144.98	54.78	35.31	37.60	32.39	20.71	5.35	13.56
5	143.15	52.88	34.17	37.02	32.19	20.50	5.00	13.44
6	141.17	50.99	33.07	36.46	31.95	20.37	4.84	13.35
7	139.24	49.09	31.91	35.88	31.68	20.22	4.66	13.26
8	137.23	47.12	30.68	35.25	31.46	20.09	4.24	13.13
9	135.24	45.16	29.50	34.67	31.18	19.91	3.97	12.99
10	133.20	43.14	28.24	34.09	30.95	19.76	3.91	12.86
11	131.14	41.08	27.02	33.44	30.70	19.57	3.58	12.76
12	129.05	38.10	25.75	32.77	30.42	19.41	3.53	12.61
13	126.95	36.88	24.45	32.14	30.17	19.25	3.27	12.46
14	124.79	34.81	23.22	31.46	29.87	19.08	3.24	12.34
15	122.58	32.70	21.94	30.79	29.61	18.90	3.04	12.16
16	120.34	30.59	20.67	30.08	29.32	18.69	2.99	11.99
17	118.04	28.52	19.47	29.39	29.05	18.51	2.83	11.87
18	115.70	26.43	18.26	28.68	28.75	18.32	2.73	11.71
19	113.32	24.43	17.09	27.92	28.46	18.12	2.64	11.48
20	110.88	22.44	15.97	27.17	28.20	17.91	2.51	11.31
21	108.39	20.59	14.86	26.42	27.84	17.72	2.45	11.16
22	105.82	18.69	13.84	25.65	27.52	17.49	2.35	10.99
23	103.19	16.96	12.80	24.90	27.20	17.25	2.27	10.80
24	100.48	15.31	11.89	24.09	26.87	17.04	2.13	10.61
25	97.70	13.74	10.98	23.31	26.53	16.89	2.03	10.44
26	94.83	12.30	10.16	22.49	26.17	16.56	1.97	10.25
27	91.89	10.91	9.36	21.72	25.82	16.33	1.88	10.06
28	88.84	9.65	8.61	20.91	25.46	16.07	1.79	9.89
29	85.69	8.52	7.94	20.19	25.07	15.81	1.69	9.70
30	82.49	7.44	7.29	19.30	24.69	15.55	1.60	9.50
31	79.18	6.47	6.70	18.53	24.31	15.26	1.50	9.32
32	75.78	5.62	6.09	17.73	23.89	14.99	1.41	9.13
33	72.29	4.83	5.62	16.96	23.47	14.69	1.34	8.97
34	68.70	4.09	5.12	16.20	23.04	14.39	1.27	8.79
35	65.02	3.48	4.66	15.48	22.62	14.08	1.21	8.61
36	61.33	2.88	4.26	14.72	22.16	13.76	1.14	8.43
37	57.56	2.42	3.87	14.03	21.68	13.45	1.05	8.26
38	53.76	1.98	3.54	13.32	21.22	13.13	0.96	8.09
39	49.97	1.61	3.17	12.68	20.73	12.76	0.90	7.91
40	46.15	1.28	2.89	12.01	20.22	12.43	0.85	7.76
41	42.47	0.98	2.60	11.38	19.74	12.09	0.79	7.61
42	38.79	0.78	2.36	10.78	19.20	11.73	0.72	7.43
43	35.29	0.56	2.11	10.20	18.67	11.37	0.67	7.27
44	31.95	0.35	1.89	9.63	18.14	11.00	0.62	7.13
45	28.73	0.28	1.67	9.09	17.58	10.63	0.57	6.98
46	25.76	0.13	1.56	8.56	17.03	10.28	0.52	6.82
47	22.92	0.07	1.34	8.09	16.46	9.90	0.47	6.67
48	20.36	0.08	1.19	7.61	15.87	9.52	0.44	6.52
49	17.99		1.03	7.18	15.30	9.14	0.42	6.38
50	15.83		0.93	6.76	14.72	8.79	0.40	6.24
51	13.81		0.82	6.36	14.17	8.42	0.38	6.11
52	12.01		0.79	5.95	13.57	8.07	0.34	5.98
53	10.41		0.64	5.57	13.00	7.74		5.85
54	8.93		0.49	5.25	12.43	7.37		5.72
55	7.62		0.47	4.90	11.87	7.04		5.58
56	6.43		0.47	4.59	11.34	6.69		5.45
57	5.40		0.40	4.29	10.77	6.38		5.33
58	4.48		0.26	4.09	10.25	6.01		5.21
59	3.68		0.24	3.74	9.73	5.71		5.09
60	2.97		0.25	3.46	9.22	5.41		4.98

Table 5
Vibrational energy level spacing ($E_v - E_{v-1}$) (in cm^{-1}) of the LiK^+ low lying states

v	$10^2\Sigma^+$	$11^2\Sigma^+$	$12^2\Sigma^+$	$13^2\Sigma^+$	$14^2\Sigma^+$	$3^2\Pi$	$4^2\Pi$	$6^2\Pi$	$7^2\Pi$
0									
1	14.66	12.49	8.67	6.03	3.07	32.68	15.69	10.81	13.71
2	14.57	12.42	8.56	5.61	2.52	32.46	15.52	10.45	13.63
3	14.47	12.35	8.47	5.23	1.91	32.24	15.32	10.16	13.47
4	14.28	12.27	8.43	4.99	1.01	32.06	15.19	9.78	13.32
5	14.24	12.20	8.37	4.71	0.63	31.85	14.97	9.45	13.23
6	14.07	12.17	8.29	4.48	0.65	31.65	14.78	9.07	13.06
7	13.98	12.07	8.22	4.26	0.63	31.43	14.56	8.70	12.91
8	13.85	12.02	8.14	4.08	0.60	31.23	14.37	8.30	12.80
9	13.70	11.94	8.06	3.84	0.58	31.03	14.14	7.88	12.62
10	13.56	11.87	7.98	3.66	0.55	30.81	13.90	7.50	12.52
11	13.42	11.81	7.91	3.46	0.54	30.60	13.70	7.07	12.37
12	13.28	11.72	7.83	3.28	0.53	30.40	13.45	6.67	12.24
13	13.14	11.65	7.75	3.10	0.52	30.18	13.21	6.17	12.11
14	13.01	11.56	7.67	2.90	0.52	29.96	12.98	5.77	11.97
15	12.86	11.48	7.56	2.70	0.51	29.75	12.73	5.32	11.80
16	12.69	11.39	7.50	2.49	0.50	29.53	12.48	4.87	11.65
17	12.54	11.30	7.41	2.29	0.49	29.33	12.25	4.42	11.53
18	12.41	11.22	7.31	2.10	0.47	29.10	12.02	3.98	11.39
19	12.24	11.14	7.22	1.90	0.43	28.86	11.75	3.51	11.22
20	12.07	11.05	7.12	1.72		28.63	11.53	3.08	11.09
21	11.91	10.95	7.02	1.52		28.42	11.25	2.69	10.93
22	11.75	10.85	6.91	1.30		28.17	11.04	2.25	10.77
23	11.58	10.75	6.81	1.08		27.97	10.76		10.63
24	11.41	10.64	6.70	0.88		27.71	10.52		10.48
25	11.24	10.53	6.58	0.70		27.48	10.28		10.35
26	11.06	10.42	6.46	0.50		27.23	10.04		10.20
27	10.88	10.30	6.32	0.26		26.98	9.82		10.04
28	10.70	10.19	6.18	0.23		26.73	9.55		9.88
29	10.50	10.06	6.02	0.21		26.49	9.35		9.74
30	10.31	9.94	5.84			26.23	9.12		9.59
31	10.11	9.81	5.58			25.98	8.90		9.44
32	9.92	9.67	2.31			25.70	8.67		9.28
33	9.74	9.53	2.99			25.42	8.46		9.12
34	9.54	9.38	4.26			25.14	8.24		8.97
35	9.34	9.23	2.66			24.86	8.04		8.82
36	9.13	9.08	3.65			24.56	7.84		8.67
37	8.93	8.92	3.85			24.29	7.63		8.53
38	8.73	8.76	3.96			23.98	7.45		8.38
39	8.53	8.59	4.04			23.65	7.24		8.22
40	8.33	8.41	4.10			23.33	7.06		8.08
41	8.12	8.23	4.14			22.99	6.87		7.95
42	7.91	8.05	4.19			22.66	6.70		7.79
43	7.70	7.86	4.21			22.30	6.53		7.66
44	7.50	7.66	4.23			21.93	6.35		7.52
45	7.30	7.47	4.27			21.54	6.17		7.37
46	7.10	7.27	4.28			21.12	6.00		7.24
47	6.90	7.06	4.28			20.70	5.85		7.09
48	6.70	6.86	4.29			20.25	5.69		6.96
49	6.51	6.65	4.29			19.77	5.52		6.82
50	6.31	6.45	4.29			19.30	5.37		6.70
51	6.12	6.24	4.28			18.77	5.26		6.57
52	5.93	6.04	4.27			18.19	5.11		6.44
53	5.72	5.84	4.26			17.60	4.93		6.31
54	5.57	5.64	4.25			16.95	4.80		6.19
55	5.40	5.44	4.23			16.28	4.66		6.06
56	5.23	5.25	4.21			15.57	4.52		5.94
57	5.01	5.06	4.19			14.81	4.39		5.81
58	4.89	4.89	4.17			14.03	4.26		5.70
59	4.72	4.71	4.14			13.19	4.13		5.58
60	4.56	4.54	4.11			12.37	4.00		5.47

4. Vibrational levels and long-range potential

The vibrational energy levels of the LiK^+ electronic states have been determined using the Numerov algorithm with 30,000 points, $R_{\min} = 4.25$ a.u., $R_{\max} = 150$ a.u. and a reduced mass $\mu = 10745.1212$ amu. In Tables 4 and 5 we report the vibrational energy level spacing for the 1–8, 10–14 $2^2\Sigma^+$ and 3, 4, 6, 7 $2^2\Pi$ states obtained using the Numerov method. Due to the long-range behavior, which has given wide wells for many potential energy curves, several

states have trapped large number of vibrational levels. The last vibrational energy levels of such states are very close to each other and may cause numerical problems in the Numerov algorithm. The difference of energy between such energy levels is very small and in some cases it is smaller than the ab initio precision it self (10^{-6} a.u.).

Furthermore, using the fit of $(E_v - D)^{1/4}$ versus v we find the total number of vibrational level trapped by each state and specially the last excited vibrational levels near the dissociation limit. For such levels the use of the cubic

Table 6

Analytical turning point position: R_c (in a.u.), vibrational energy: E_v and vibrational level spacing: $(E_{v+1} - E_v)$ of the $2^2\Sigma^+$ state of LiK^+

v	$R_c(v)$ (a.u.)	$E(v)$ (a.u.)	$E(v)$ (cm^{-1})	$E_{v+1} - E_v$ (a.u.)	$E_{v+1} - E_v$ (cm^{-1})
49	195.4347876038	-0.1595150925	-35009.5749		
50	275.5310571335	-0.1595150185	-35009.5587	0.0000000740	0.0162478958
51	466.8722519555	-0.1595149965	-35009.5539	0.0000000220	0.0048384664
52	1527.9487444168	-0.1595149935	-35009.5532	0.0000000030	0.0006621538

Table 7

Analytical turning point position: R_c (in a.u.), vibrational energy: E_v and vibrational level spacing: $(E_{v+1} - E_v)$ of the $5^2\Sigma^+$ state of LiK^+

v	$R_c(v)$ (a.u.)	$E(v)$ (a.u.)	$E(v)$ (cm^{-1})	$E_{v+1} - E_v$ (a.u.)	$E_{v+1} - E_v$ (cm^{-1})
101	157.2720369694	-0.0741581183	-16275.8530		
102	168.1034469784	-0.0741573897	-16275.6931	0.0000007286	0.1599179876
103	180.5371369723	-0.0741567970	-16275.5630	0.0000005927	0.1300776122
104	194.9570399576	-0.0741563222	-16275.4588	0.0000004748	0.1042028100
105	211.8803990522	-0.0741559486	-16275.3768	0.0000003737	0.0820107298
106	232.0211278230	-0.0741556605	-16275.3136	0.0000002880	0.0632185204
107	256.3931036256	-0.0741554439	-16275.2661	0.0000002166	0.0475433304
108	286.4862027632	-0.0741552858	-16275.2313	0.0000001581	0.0347023088
109	324.5827892843	-0.0741551746	-16275.2069	0.0000001112	0.0244126043
110	374.3654513038	-0.0741550999	-16275.1905	0.0000000747	0.0163913656
111	442.1853206815	-0.0741550527	-16275.1802	0.0000000472	0.0103557415
112	540.0140041202	-0.0741550252	-16275.1742	0.0000000274	0.0060228809
113	693.4272197905	-0.0741550111	-16275.1711	0.0000000142	0.0031099324
114	968.5971186626	-0.0741550050	-16275.1697	0.0000000061	0.0013340449
115	1605.8334683796	-0.0741550031	-16275.1693	0.0000000019	0.0004123672
116	4693.9946575738	-0.0741550028	-16275.1692	0.0000000003	0.0000620480

Table 8

Analytical turning point position: R_c (in a.u.), vibrational energy: E_v and vibrational level spacing: $(E_{v+1} - E_v)$ of the $6^2\Sigma^+$ state of LiK^+

v	$R_c(v)$ (a.u.)	$E(v)$ (a.u.)	$E(v)$ (cm^{-1})	$E_{v+1} - E_v$ (a.u.)	$E_{v+1} - E_v$ (cm^{-1})
93	152.0529232369	-0.0637538349	-13992.3729		
94	161.7687640300	-0.0637529931	-13992.1882	0.0000008418	0.1847603406
95	172.8109993325	-0.0637522980	-13992.0356	0.0000006950	0.1525407193
96	185.4711443883	-0.0637517317	-13991.9113	0.0000005664	0.1243043603
97	200.1328931646	-0.0637512770	-13991.8115	0.0000004547	0.0997883421
98	217.3116800275	-0.0637509183	-13991.7328	0.0000003587	0.0787297429
99	237.7165296882	-0.0637506409	-13991.6719	0.0000002773	0.0608656413
100	262.3503630665	-0.0637504317	-13991.6260	0.0000002093	0.0459331157
101	292.6798794588	-0.0637502783	-13991.5923	0.0000001534	0.0336692444
102	330.9386795994	-0.0637501698	-13991.5685	0.0000001085	0.0238111060
103	380.7038831621	-0.0637500964	-13991.5524	0.0000000733	0.0160957788
104	448.0850832194	-0.0637500497	-13991.5422	0.0000000467	0.0102603413
105	544.4474351081	-0.0637500221	-13991.5361	0.0000000275	0.0060418719
106	693.6110536758	-0.0637500077	-13991.5329	0.0000000145	0.0031774491
107	955.3509228259	-0.0637500013	-13991.5315	0.0000000064	0.0014041511
108	1534.3509506957	-0.0637499992	-13991.5311	0.0000000021	0.0004590565
109	3894.8846332649	-0.0637499988	-13991.5310	0.0000000004	0.0000792437

interpolation and the Numerov propagation methods, employed to find the wave function, leads to serious numerical difficulties in that region where the potential energy difference between two ab initio calculated points tends to zero and the difference between two neighbor turning points becomes very large. By an inspection of the potential energy data the difference between the energy of two closed points at large distances and for higher excited states is about 10^{-6} a.u., which is the precision of the ab initio calculation.

Fortunately, using the semiclassical extrapolation we can get the missed vibrational energy levels and the total number of trapped vibrational levels. According to the WKB semiclassical approximation, the total number of the vibrational levels corresponds to the integer part of v_D . We find for the 1–8, 10–14 $2\Sigma^+$ and 3, 4, 6, 7 2Π studied states, respectively, 72, 49, 62, 89, 101, 93, 53, 122, 108, 105, 132, 30, 20, 103, 105, 23, and 128 total vibrational levels. Tables 6–9 present the missed vibrational levels in the Numerov calculation and their turning points for some

Table 9

Analytical turning point position: R_c (in a.u.), vibrational energy: E_v and vibrational level spacing: $(E_{v+1} - E_v)$ of the $11^2\Sigma^+$ state of LiK^+

v	$R_c(v)$ (a.u.)	$E(v)$ (a.u.)	$E(v)$ (cm^{-1})	$E_{v+1} - E_v$ (a.u.)	$E_{v+1} - E_v$ (cm^{-1})
105	151.7675079153	-0.0386212428	-8476.3973		
106	154.9842847588	-0.0386186482	-8475.8278	0.0000025946	0.5694535578
107	158.3403763426	-0.0386162135	-8475.2934	0.0000024348	0.5343725934
108	161.8450333150	-0.0386139318	-8474.7927	0.0000022816	0.5007628708
109	165.5083438660	-0.0386117967	-8474.3241	0.0000021351	0.4685928723
110	169.3413307104	-0.0386098018	-8473.8863	0.0000019949	0.4378310803
111	173.3560618653	-0.0386079408	-8473.4778	0.0000018610	0.4084459773
112	177.5657775695	-0.0386062076	-8473.0974	0.0000017333	0.3804060457
113	181.9850361543	-0.0386045961	-8472.7437	0.0000016115	0.3536797677
114	186.6298822537	-0.0386031005	-8472.4155	0.0000014955	0.3282356259
115	191.5180414485	-0.0386017152	-8472.1115	0.0000013853	0.3040421025
116	196.6691463214	-0.0386004346	-8471.8304	0.0000012806	0.2810676801

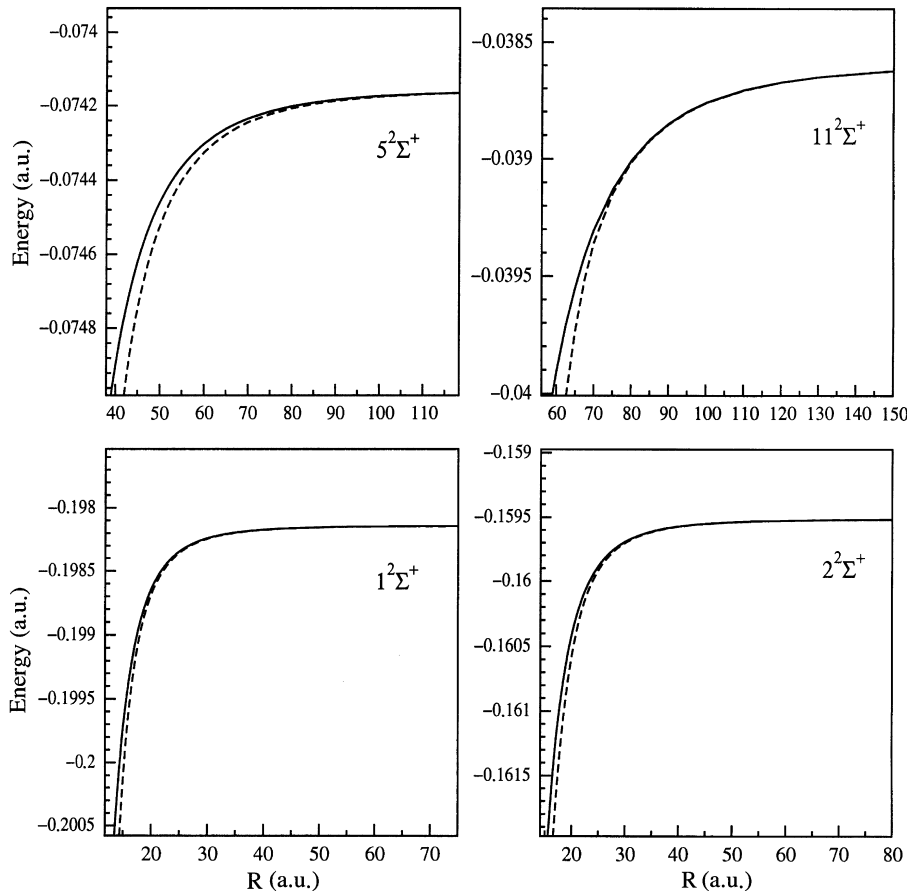


Fig. 3. Comparison between the ab initio calculated and the long-range analytical potential energies for 1, 2, 5, and $11^2\Sigma^+$ electronic states.

vibrational levels associated to the 1, 2, 5 and $11^2\Sigma^+$ states. It seems that the last vibrational energy levels are very close to each others and the difference between them is much smaller than 1 cm^{-1} . We remark that the vibrational energy levels not found by the Numerov algorithm have turning points at a distance larger than $R_{\text{max}}=150$ a.u. In same cases the turning point of a vibrational energy level is about some thousands of a.u. That means that finding them by the Numerov algorithm needs the determination of the potential energy at very large distances where the difference between two calculated points will be much smaller than 10^{-6} a.u. This represents an impossible task as the accuracy of the ab initio energy is equal to 10^{-6} a.u. Therefore, in the asymptotic region, the propagation of the wave function using the Numerov algorithm will cause dramatic numerical problems.

In order to test the accuracy of the evaluated polarizabilities, we have reproduced the potential energy curves of 1, 2, 5 and $11^2\Sigma^+$ electronic states using the analytical expression of Eq. (1). As it seems from Fig. 3, there is a very good agreement between our ab initio calculated and the analytical energies. Such agreement becomes better for large distance where the behavior of the potential energy is corresponding to a pure charge–dipole interaction and no chemical effects are acting. The very good agreement between the analytical curves using the extracted polarizabilities and the calculated ab initio curves, shows the good accuracy of our polarizabilities using a simple approach based on the WKB semiclassical approximation.

5. Conclusion

Accurate long-range potentials have been obtained using the WKB approximation by analyzing the vibrational level spacings of the LiK^+ electronic states dissociating into $\text{Li}(2s, 2p, 3s, 3p, 3d, 4s, \text{ and } 4p) + \text{K}^+$ and $\text{Li}^+ + \text{K}(4s, 4p, 5s, 3d, 5p, 4d, \text{ and } 6s)$. The plot of $(E_v - D)^{1/4}$ versus v has shown a pure linear behavior. A least squares fit of this linear law has allowed us to extract rather accurately the v_D and C_4 ($C_4 = \alpha/2$) constants from which all vibrational levels near the dissociation limit and also the related turning points have been calculated. The calculation of the polarizabilities of np and nd Li and K atomic levels, using $1/R^4$ long-range behavior of their related potential energy curves has given wrong values in comparison with the theoretical values of the recent work of Magnier et al. [22]. It seems that the long-range behavior of the potential interaction energies of the electronic states dissociating into $\text{Li}(np, nd)$ and $\text{K}(np, nd)$ is governed by both $1/R^3$ and $1/R^4$, corresponding to the interac-

tion between the alkali ion charge and the atom quadrupole. We have interpolated such potential energy curves by the analytical form $\pm \frac{q}{R^3} - \frac{\alpha}{R^4}$. This leads to reasonable values which are in good agreement with the work of Magnier et al. Using the extracted C_4 constants, we have reproduced the long-range potential energy curves. The agreement between the ab initio calculated potential and the analytical points has shown the good accuracy of the obtained atomic polarizabilities for the Li and K ground state and for numerous excited levels.

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