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The low-lying adiabatic states of the K_2^+ alkali dimer

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Abstract

Despite the simplicity of the K_2^+ alkali dimer with a single active electron, comparison of the *ab-initio* results of Berriche *et al.* [1] with those of Magnier and Frécon [2] based on a model potential approach reveals a number of serious disagreement concerning several excited states. In particular, the $5^2\Sigma_u^+$, $6^2\Sigma_g^+$, $6^2\Sigma_u^+$, $7^2\Sigma_g^+$, $7^2\Sigma_u^+$, $3^2\Pi_g$, $4^2\Pi_g$ and $2^2\Delta_u$ states which are found to be repulsive by Magnier and Frécon, but attractive when *ab-initio* techniques are employed.

To clarify the origin of this disagreement, the adiabatic energies and spectroscopic constants are re-computed for the low-lying states of the K_2^+ alkali dimer within a model potential framework. Contrary to the claims of Magnier and Frécon, the new results based on a model potential approach agree well with the *ab-initio* ones.

Keywords: model potential, K_2^+, *ab-initio*, adiabatic energies, molecular spectroscopic constants

1. Introduction

During the past few decades, several studies in quantum chemistry have been developed to obtain an accurate description of potential energy surfaces of excited electronic states [3, 4, 5, 6]. Such surfaces provide the starting point for the investigation either of non-adiabatic effects via avoided crossings or of the dissociation into different fragments along a minimum energy path in presence of an external electromagnetic field.

In the particular case of diatomic molecules, potential energy surfaces simply become potential energy curves, which can be computed by solving the electronic time-independent Schrodinger equation for different internuclear separations in the Born-Oppenheimer approximation [7]. Morever, for diatomic molecular ions formed by a neutral atom and an ion, it is well known that the corresponding potential energy curves generally exhibit a certain number of avoided crossings which can be exploited to obtain cross sections of charge transfer and excitation processes which may occur between different molecular adiabatic states.

Over the past few years, potential energy curves of several diatomic molecules have been investigated with a special focus both on neutral and ionized alkali-dimer systems

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[8, 9, 10, 11]. This particular interest is generally due to the recent development in the cold collision dynamics involving alkali diatomic systems.

In the present paper, we are concerned with the K_2^+ alkali-dimer molecular cation, which has been the subject of several theoretical and experimental studies. From the experimental perspective, according to the measurements of Stwalley and Wang [12] using a spectroscopic technique of the photoassociation of ultra cold atoms, the estimated ground state dissociation energy D_e of the K_2^+ ion was found to be 6670 cm^{-1}, while in an experimental work using a supersonic alkali-metal beam with a sequential two photon ionization technique, developed by Leutwyler *et al.* [13], the dissociation energy was found to be equal to 6404 cm^{-1}. On the other hand, according to Broyer *et al.* [14] who employed a technique of resonant two and three-photon ionization, the K_2^+ ground state $1^2\Sigma_g^+$, has harmonic and anharmonic vibration constants, ω_e=73.40 cm^{-1} and $\omega_e\chi_e$= 0.2 cm^{-1}, respectively.

From the theoretical point of view, multi-electron *ab-initio* calculations have been performed by Konowalow and Rosenrantz [15] to compute the electronic structure of a few light alkali diatomic molecules and their molecular cations, such as Li_2^+ and Na_2^+. Their calculated data was then scaled to predict qualitative results for the K_2^+ molecular ion. On the other hand, Ilyabaev and Kaldor [16] used a Fock-space open-shell coupled cluster approach to compute the potential energy of the three lowest states, while Valance [17] employed a Hellmann-type pseudopotential to generate the potential energy curves of the six lowest Σ^+ states. In a recent study, electron affinity calculations based on the equation of motion coupled cluster method has been employed by Skupin *et al.* [18] to accurately describe the six (four Σ^+ and two Π) lowest lying electronic states.

A theoretical investigation of the first 58 adiabatic states including spin-orbit effects has been performed by Jraij *et al.* [19], whereas in an extensive study, Berriche *et al.* [1] employed an *ab-initio* approach to compute the adiabatic energies of states dissociating up to K^++K(6s) limit, for a wide range of internuclear separations ($2 \leq R \leq 92$) a.u.

In addition to the *ab-initio* and pseudo potential methods which provide most available data describing the K_2^+ ion, model potential techniques were employed by Henriet and Masnou-seeuws [20] to generate the spectroscopic constants of the ground state. In an alternative study also based on model potential approach, Henriet [21] has been successful in providing the adiabatic energies of the first excited states for short and intermediate internuclear separations up to 20 a.u. But to the best of our knowledge, the most extensive work exploiting model potential techniques remains the one by Magnier and Frécon [2] who used a potential of Klapisch [22] to compute adiabatic energies for states dissociating up to K^++K(6s) limit for short and intermediate internuclear distances, 4 $\leq R \leq$ 35 a.u.

While for the ground state studies based on different approaches indicate a global agreement, for several excited states an important disagreement is observed between theoretical results. For example, an important disagreement is observed when comparing the *ab-initio* results of Berriche *et al.* [1] and those of Magnier and Frécon [2] based on model potential techniques. In particular, the $5^2\Sigma_u^+$, $6^2\Sigma_g^+$, $6^2\Sigma_u^+$, $7^2\Sigma_g^+$, $7^2\Sigma_u^+$, $3^2\Pi_g$, $4^2\Pi_g$ and $2^2\Delta_u$ states which are found to be repulsive by Magnier and Frécon, whereas these states exhibit a well pronounced energy minimum when *ab-initio* [1] techniques are employed.

As shown by Rabli and McCarroll [23, 24] in previous studies treating the Li_2^+ and $NaLi^+$ molecular ions, in principle model potential methods should be suitable for the

Table 1: Comparison of calculated and experimental energy levels in cm^{-1} of different states in the dissociation limit.

Level	Present work	[2]	[1]	Exp [28]
K^++ K(4s)	0.00	0.00	0.00	0.00
K^++ K(4p)	13092.54	13077.61	13022.99	13042.90
K^++ K(5s)	21010.53	20980.67	21018.02	21026.55
K^++ K(3d)	21665.98	21575.01	21535.54	21536.99
K^++ K(5p)	24712.41	24670.70	24750.85	24720.14
K^++ K(4d)	27438.61	27366.94	27417.26	27398.15
K^++ K(6s)	27461.49	27424.01	27451.93	27450.71

description of the K_2^+ system without difficulties. In the present work we re-investigate the K_2^+ system within a model potential framework to generate the adiabatic energy curves and the molecular spectroscopic constants of molecular states dissociating up to the K^++ K(6s) limit. Our aim is to clarify whether this disagreement between the *ab-initio* and model potential methods originates from some conceptual defect of the model potential technique or whether there is some source of error in the calculations of Magnier and Frécon [2].

Except where stated, atomic units will be used throughout.

2. Theory

Model potential methods have been widely employed in describing bound states of alkaline atoms. In the particular case of the K_2^+ molecular ion, the interaction of the valence electron with the closed shell $K^+(3p^6)$ is described by a model potential proposed by Klapisch [22] which has been used in a previous work by Magnier and Frécon [2]:

$$V_{model}(r) = -\frac{q}{r} - \frac{Z-1}{r}(e^{-ar} + cre^{-br}), \tag{1}$$

where r denotes the radial distance of the electron form the nucleus, $q = 1$ the ionic core charge and $Z = 19$ the atomic number. The parameters (a,b,c) shown in Table 2 are in units of inverse length au^{-1}, and have 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 Potassium atom.

The description of the energies in the atomic limit, is indeed crucial, and has already been adequately discussed in much of the earlier work on model potentials notably by McCarroll and Valiron [31, 32]. Other aspects of the model potential approach were treated by several authors [33, 34, 35] on the introduction of other non-local constraints, such as the orthogonality to the inner orbitals. However, in the present study, we mainly recall that the aim of the model potential is to represent in a physically meaningful way the ground and excited states with a reasonable precision. Since spin-orbit interactions

q	Z	a	b	c
1	19	3.474	1.725	0.588333

Table 2: Klapisch model potential parameters [22]. a,b and c are given in units of inverse length (1/au).

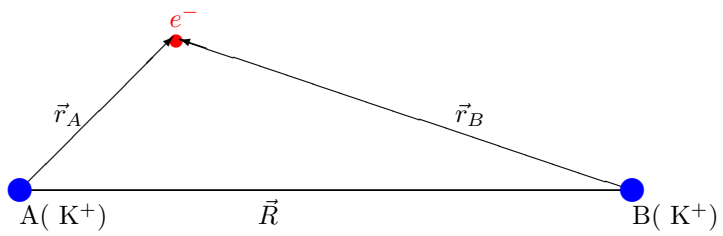

Figure 1: Relative coordinates for the active electron.

have been neglected (Hamiltonian in Eq (3) does not contain any spin dependence), the precision of our computed energies in the asymptotic limit and which are shown in Table 1, is adequate for the particular applications of this work.

Fixing the two Potassium cores at A and B positions respectively as shown in Fig. 1, the K_2^+ molecular cation is then treated as a set of two closed shell $K^+(3p^6)$ cores and a single active electron moving in the field created by the two ionic cores. The electronic Hamiltonian is given by

$$H_e = T + V_{model}(r_A) + V_{model}(r_B) + U_{core}, \tag{3}$$

where T denotes the electronic kinetic energy operator, r_A and r_B the radial distances of the active electron from the cores K^+ respectively. U_{core} is mainly The nuclei repulsion U_{core} term is modified by a polarization term, namely:

$$U_{core} = \frac{1}{R} - \frac{\alpha_d}{R^4} - \frac{\alpha_q}{R^6}, \tag{4}$$

where α_d and α_q are the dipole and quadrupolar polarizabilities, respectively, which have been used in the work of Magnier and Frécon [2], $\alpha_d = 5.354$ a.u [25] and $\alpha_q = 4.69$ a.u [26].

The spectrum of the effective Hamiltonian H_e defined in Eq (3) is determined by conventional variational techniques, using a basis set of Slater-type orbitals ψ^{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:

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

where N denotes a normalization factor, ϵ a parameter that takes the values ± 1 depending on whether the orbital is centered on nucleus A or nucleus B, (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 $\mathbf{R}$) and $\Lambda = \mid m \mid$=0,1,2,... for Σ^+, Π and Δ molecular states respectively.

3. Results

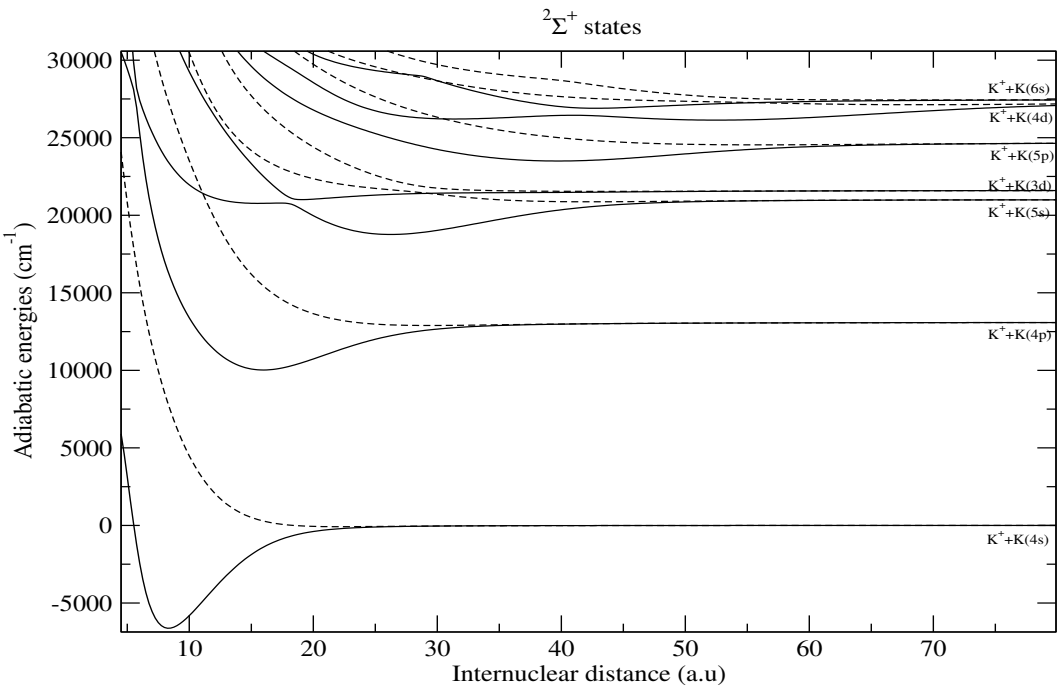

Figure 2: K_2^+ potential energy curves given with respect to the ground state dissociation limit. Σ_g^+ in solid lines, Σ_u^+ in dashed lines.

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
$1^2\Sigma_g^+$	8.33	6630	0	73.04	0.201	0.0444	Present work
	8.58	6454	0	73.05	0.14	0.041818	[1]
	8.3	6685	0	73.2			[2]

		6670					[12]
	8.31	6404					[13]
				73.40	0.2		[14]
	7.9	6130	0				[17]
	8.384	6481	0	72.4	0.13		[18]
	8.39	6460	0	75			[21]
	8.53	6589	0	73.7			[25]
	8.47	6690	0	73.70			[27]
	8.60	6573		72.4	0.25		[16]
	8.49	6537	0	72			[29]
$1^2\Sigma_u^+$	22.18	80	6550	5.72	0.102	0.0063	Present work
	22.43	80	6374	5.72	0.13	0.006124	[1]
	22.55	80					[2]
	22.31	88.7	6486	9.25	0.04		[16]
	22.398	82	6511	5.7	0.11		[18]
$2^2\Sigma_g^+$	15.96	3070	16652	28.24	0.065	0.0120	Present work
	16.02	3038	16446	28.03	0.04	0.011994	[1]
	16.00	3048					[2]
	15.737	2909	16643	30.2	0.04		[18]
$2^2\Sigma_u^+$	29.33	199	19522	5.83	0.043	0.0036	Present work
	29.39	212	19272	5.83	0.05	0.003565	[1]
	30.25	188					[2]
	28.913	182	19370	6.1	0.06		[18]
$3^2\Sigma_g^+$	26.22	2249	25391	17.10	0.033	0.0045	Present work
	26.3	2201	25280	16.68	0.02	0.004451	[1]
	26.25	2233					[2]
$3^2\Sigma_u^+$	42.39	141	27498	3.99	0.028	0.0017	Present work
	42.6	154	27326	3.98	0.03	0.001697	[1]
	41.75	138					[2]
$4^2\Sigma_g^+$	19.04	617	27637	27.58	0.308	0.0085	Present work
	19.72	427	27573	18.7	0.24	0.007916	[1]
	19.25	587					[2]
$4^2\Sigma_u^+$	43.9	83	28170	2.17	0.014	0.0016	Present work
	45.27	72	27929	4.31	0.29	0.001502	[1]
	49.25	73					[2]
$5^2\Sigma_g^+$	39.74	1211	30128	9.13	0.017	0.0020	Present work
	39.83	1256	29997	9.03	0.01	0.001942	[1]
	39.5	1202					[2]
$5^2\Sigma_u^+$	56.04	169	31170	2.91	0.012	0.0009	Present work
	56.35	232	31021	3.04	0.01	0.00097	[1]
	Repulsive						[2]
$6^2\Sigma_g^+$	31.39	1200	32836	9.56	0.019	0.0031	Present work
	31.84	838	33176	6.92	0.05	0.003038	[1]
	52.48	1272	32764	8.44	0.0140131	0.0011179	Present work
	53.17	1130	32742	6.55	0.05	0.003038	[1]
	Repulsive						[2]

$6^2\Sigma_u^+$	68.72	279	33757	3.15	0.009	0.0007	Present work
	65.75	243	33628	10.63	0.05	0.000712	[1]
	70.72	259	33612	8.23	0.05	0.000712	[1]
	Repulsive						[2]
$7^2\Sigma_g^+$	42.74	562	33528	11.26	0.056	0.0017	Present work
	42.24	394	33521	11.25	0.13	0.001726	[1]
	Repulsive						[2]
$7^2\Sigma_u^+$	67.74	26	34064	1.32	0.017	0.0007	Present work
	70.27	19	33895	1	0.04	0.000623	[1]
	Repulsive						[2]

3.1. Σ^+ *states*

We generated the potential energy curves of the $^2\Sigma^+$ states dissociating up to the K^++K(6s) limit. Corresponding graphics are plotted in Fig. 2, while the spectroscopic constants are listed and compared to available values issued from different approaches in Table 3.

For the $1^2\Sigma_g^+$ ground state correlated to K^++K(4s) in the asymptotic limit, present work yields a dissociation energy D_e=6630 cm^{-1}, an equilibrium distance R_e=8.33 a.u, vibration constants ω_e=73.04 cm^{-1} and $\omega_e\chi_e$= 0.201 cm^{-1}. Those values may be compared to the *ab-intio* results [1], D_e=6454 cm^{-1}, R_e=8.58 a.u, ω_e=73.05 cm^{-1} and $\omega_e\chi_e$= 0.14 cm^{-1}. On the other hand, as indicated in Table 3, it is interesting to note that our dissociation energy compares well to the experimental value D_e=6670 cm^{-1}, obtained by Stwalley *et al.* [12].

For the first excited state $1^2\Sigma_u^+$ also correlated to K^++K(4s) in the asymptotic limit, the analysis of our potential energy curve indicates the existence of an energy minimum occurring at an equilibrium distance R_e= 22.18 a.u, with a corresponding dissociation energy D_e=80 cm^{-1}. As shown in Table 3, these values compare well to the ones issued from different approaches [1, 2, 18]. Our vibration constants ω_e=5.72 cm^{-1} and $\omega_e\chi_e$=0.102 cm^{-1} are in perfect agreement with those based on *ab-initio* method [1], ω_e=5.72 cm^{-1} and $\omega_e\chi_e$=0.13 cm^{-1}.

A good agreement is also observed between our $2^2\Sigma_g^+$ state spectroscopic constants and those resulting from previous studies [1, 2]. Present study yields a dissociation energy D_e=3070 cm^{-1} and an internuclear equilibrium distance R_e=15.96 a.u. These values may be compared to the *ab-initio* ones [1], D_e=3038 cm^{-1}, R_e=16.02 a.u and to the ones resulting from a model potential approach [2], D_e=3048 cm^{-1} and R_e=16.00 a.u.

For the $2^2\Sigma_u^+$ state correlated to K^++K(4p) in the asymptotic limit, an energy minimum is observed at R_e= 29.33 a.u, with a corresponding dissociation energy D_e=199 cm^{-1}. Our vibration constants ω_e=5.83 cm^{-1} and $\omega_e\chi_e$=0.043 cm^{-1} compare favorably with the *ab-initio* results [1], ω_e=5.83 cm^{-1} and $\omega_e\chi_e$=0.05 cm^{-1}.

The $3^2\Sigma_u^+$ and $3^2\Sigma_g^+$ states are correlated to K^++K(5s) in the asymptotic limit. As predicted by previous studies, present work shows that both states are attractive with spectroscopic constants listed in Table 3, that compare favorably with values resulting from other different theoretical approaches [1, 2].

For both states $4^2\Sigma_g^+$ and $4^2\Sigma_u^+$ which are correlated to K^++K(3d) in the asymptotic limit, we have found an equilibrium distances R_e= 19.04 a.u and R_e=43.9 a.u respectively. A good agreement is also observed between our $4^2\Sigma_u^+$ and $4^2\Sigma_g^+$ spectroscopic constants and those based on an *ab-initio* approach [1].

The potential energy curve of our $5^2\Sigma_g^+$ state correlated to K^++K(5s) in the asymptotic limit, exhibits an energy minimum at R_e=39.74 a.u with a dissociation energy D_e=1211 cm^{-1}. As shown in Table 3, spectroscopic constants obtained in the present work are in good agreement with values resulting from other different theoretical approaches.

According to the *ab-initio* studies of Berriche [1], the $5^2\Sigma_u^+$ state is attractive, whereas Magnier and Frécon [2] employing model potential techniques described a such state as completely repulsive. In the present study, our potential energy curve has an energy minimum occurring at an equilibrium internuclear distance R_e=56.04 a.u, with a corresponding dissociation energy D_e=169 cm^{-1}. Those may be compared to the *ab-initio* values [1], R_e=56.35 a.u and D_e=232 cm^{-1}. Equally, our vibration constants ω_e=2.91 cm^{-1} and $\omega_e\chi_e$=0.012 cm^{-1} compare well to the *ab-initio* results [1], ω_e=3.04 cm^{-1} and $\omega_e\chi_e$=0.01 cm^{-1}.

Another state which has been the subject of disagreement concerns the $6^2\Sigma_g^+$ state correlated to K^++K(4d) in the dissociation limit. The analysis of our potential energy curve shows the existence of two minima. Therefore, contrary to Magnier and Frécon claims, as predicted by other *ab-initio* methods [1], our model potential approach confirms the attractive character of the $6^2\Sigma_g^+$ state. As indicated in Table 3, our $6^2\Sigma_g^+$ state has an energy minimum in the inner region, occurring at R_e=31.39 a.u, with a corresponding dissociation energy D_e=1200 cm^{-1}, vibration constants ω_e = 9.56 cm^{-1} and $\omega_e\chi_e$= 0.019 cm^{-1}. Morever, for the minimum located in the outer region, we obtained an equilibrium distance R_e=52.48 a.u with a well depth D_e=1272 cm^{-1}. Those to be compared to the ab-initio values R_e=53.17 a.u and D_e=1130 cm^{-1}.

For the states $7^2\Sigma_g^+$ and $7^2\Sigma_u^+$ contrary to Magnier and Frécon [2] who concluded that such states are repulsive, our model potential results clearly indicate that $7^2\Sigma_g^+$ and $7^2\Sigma_u^+$ are attractive as predicted by *ab into* approach [1]. We found an equilibrium distance R_e= 42.74 a.u with an dissociation energy D_e= 562 a.u for the $7^2\Sigma_g^+$ state, while for the $7^2\Sigma_u^+$ state our equilibrium distance and dissociation energy are respectively R_e= 67.74 a.u and D_e= 26 a.u.

3.2. Π *states*

Calculations have also been carried out for the first eight $^2\Pi$ states for internuclear separations up to 80 a.u. Corresponding graphics are plotted in Fig. 3, while the spectroscopic constants are listed and compared to available values issued from different approaches in Table 4.

Our potential energy curve for the $1^2\Pi_g$ state does not exhibit any minimum. Therefore, as predicted by previous studies based on different methods, our $1^2\Pi_g$ state correlated to K^++K(4p) in the dissociation limit, is purely repulsive.

On the other hand, for the $1^2\Pi_u$ state also correlated to K^++K(4p) in the dissociation limit, present study yields a dissociation energy D_e=2652 cm^{-1} and an equilibrium distance R_e= 9.58 a.u. Those may be compared to the *ab-initio* results [1], D_e=2367 cm^{-1} and R_e= 9.96 a.u and to those employing model potential approach [2], D_e=2682 cm^{-1} and R_e= 9.5 a.u.

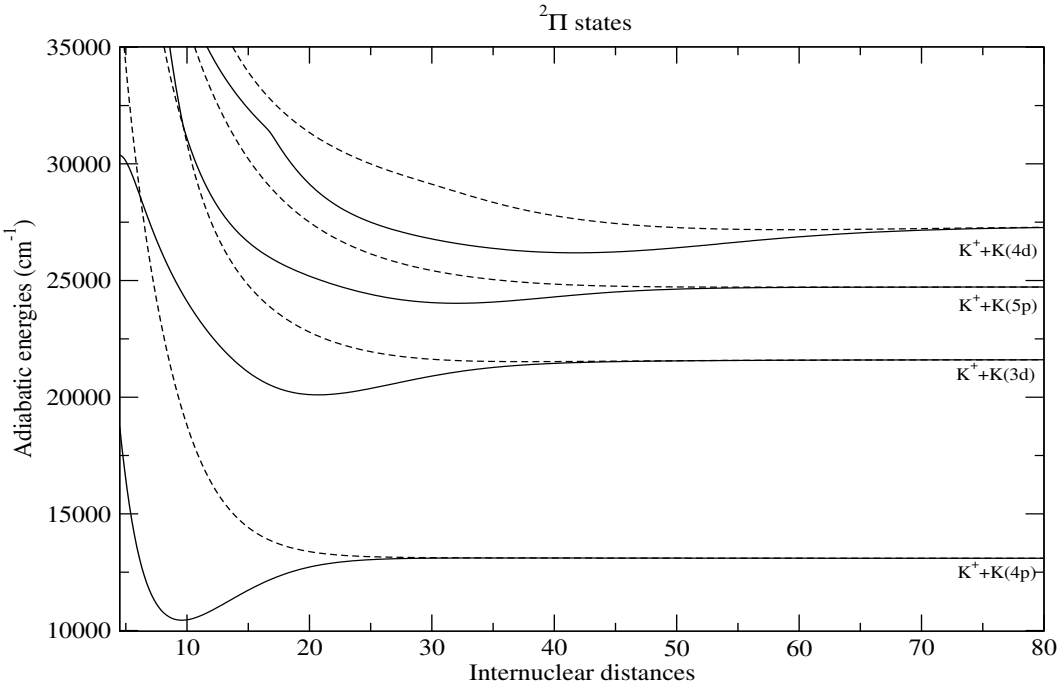

Figure 3: K_2^+ potential energy curves given with respect to the ground state dissociation limit. Π_u in solid lines, Π_g in dashed lines.

The $2^2\Pi_g$ and $2^2\Pi_u$ states are correlated to K^++K(3d) in the asymptotic limit. In the present study, as indicated in Table 4, both states have been found to be attractive with spectroscopic constants which compare well with other values issued from previous works .

Another disagreement between the *ab-initio* results [1] and those based on model potential approach [2] concerns the $3^2\Pi_g$ state, and which has been sorted out in the present study. Contrary to the conclusion of Magnier and Frécon [2], present results agree with the *ab-initio* ones. Our potential energy curve has an energy minimum occurring at R_e= 58.03 a.u with a very weak dissociation energy D_e=2 cm^{-1}, while the *ab-initio* values [1] are R_e= 57.92 a.u. and D_e=5 cm^{-1}.

For the $3^2\Pi_u$ state, present work yields a dissociation energy D_e =691 cm^{-1} and an equilibrium distance R_e=32.00 a.u. These values may be compared to the *ab-initio* ones [1], D_e=615 cm^{-1} and R_e=32.22 a.u, and to the previous ones based on model potential approach [2], D_e=681 cm^{-1} and R_e=32 a.u. As indicated in Table 4, our vibration constants ω_e=9.42 cm^{-1} and $\omega_e\chi_e$= 0.032 cm^{-1}, are slightly different from the *ab-initio* values [1], ω_e=8.32 cm^{-1} and $\omega_e\chi_e$= 0.01 cm^{-1}

The $4^2\Pi_g$ correlated to K^++K(3d) in the asymptotic region, has also been a subject of disagreement between *ab-initio* results [1] and model potential ones [2]. Present investigation clearly indicates that $4^2\Pi_g$ potential energy curve has an energy minimum occurring at R_e= 59.34 a.u, with a corresponding dissociation energy D_e= 210 cm^{-1}. These values are in agreement with *ab-initio* results [1], R_e=60.69 a.u and D_e=198 cm^{-1}.

As indicated in Table 4, our equilibrium distance R_e= 41.75 a.u and dissociation energy D_e=1202 cm^{-1} for the $4^2\Pi_u$ state, compare well to previous results particularly to the ones by Magnier and Frécon [2] giving, D_e=1216 cm^{-1} and an equilibrium distance R_e=41.75 a.u. Present study also gives vibration constants ω_e=6.96 cm^{-1} and $\omega_e\chi_e$= 0.010 cm^{-1}, which compare favorably with the *ab-initio* values [1], ω_e=7.4 cm^{-1} and $\omega_e\chi_e$=0.01 cm^{-1}.

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
$1^2\Pi_g$	Repulsive						Present work
	Repulsive						[1]
	Repulsive						[2]
	Repulsive						[18]
$1^2\Pi_u$	9.58	2652	17072	36.42	0.125	0.0336	Present work
	9.96	2367	17113	35.16	0.29	0.031017	[1]
	9.5	2682	17066	37.86			[2]
	10.41	2218	16838	31.76	0.00		[16]
	9.552	2463	17089	40.1	0.09		[18]
$2^2\Pi_g$	37.92	89	28154	2.56	0.019	0.0021	Present work
	38.47	81	27910	2.94	0.03	0.002081	[1]
	38.00	88					[2]
$2^2\Pi_u$	20.68	1511	26730	14.28	0.034	0.0072	Present work
	20.9	1376	26619	16.11	0.03	0.007047	[1]
	20.75	1504					[2]
$3^2\Pi_g$	58.03	2	31346	0.81	0.084	0.0009	Present work
	57.92	5	31206	1.11	0.04	0.000918	[1]
	Repulsive						[2]
$3^2\Pi_u$	32.00	691	30654	9.42	0.032	0.0030	Present work
	32.22	615	30595	8.32	0.01	0.002967	[1]
	32	681					[2]
$4^2\Pi_g$	59.34	210	33809	2.44	0.007	0.0009	Present work
	60.69	198	33674	2.76	0.01	0.000836	[1]
	Repulsive						[2]
$4^2\Pi_u$	41.75	1202	32817	6.96	0.010	0.0018	Present work
	42.37	983	32889	7.4	0.01	0.001716	[1]
	41.75	1216					[2]

3.3. Δ states

We generated the adiabatic energies of the $^2\Delta$ states for internuclear distances up to 80 a.u. Our energy curves are plotted in Fig. 4, while the corresponding spectroscopic constants are listed and compared to available data resulting from different approaches in Table 5.

Our potential energy curve relative to the $1^2\Delta_g$ state exhibits an energy minimum occurring at an internuclear distance R_e= 16.15 a.u, with a corresponding dissociation energy D_e= 164 cm^{-1}. While these values compare favorably to those using a model potential approach of Magnier and Frécon [2] and Henriet [21], a difference of 140 cm^{-1} is observed when comparison is made with *ab-initio* results [1] which seem to underestimate the dissociation energy value.

On the other hand, while our $1^2\Delta_u$ state is repulsive as predicted by previous studies, our potential energy curve for the $2^2\Delta_g$ state, exhibits an energy minimum occurring at an equilibrium internuclear distance R_e=28.79 a.u, with a corresponding dissociation energy D_e=1189 cm^{-1}. Those to be compared to the *ab-initio* results [1], R_e = 30.65 a.u and D_e=698 cm^{-1}.

As previously mentioned, the $2^2\Delta_u$ state correlated in the asymptotic limit to K^++K(4d) has been the subject of a disagreement, when comparing *ab-initio* results [1] and previous model potential [2] ones. Contrary to the previous model potential results [2], our study clearly indicates that the $2^2\Delta_u$ state is attractive with a dissociation energy D_e=67 cm^{-1} and an internuclear equilibrium distance R_e=53.50 a.u. These values compare favorably to the *ab-initio* ones [1], R_e=55.82 a.u and D_e=40 cm^{-1}.

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
$1^2\Delta_g$	16.15	164	28051	10.90	0.181	0.0118	Present work
	17.92	25	27971	9.43	0.1	0.009593	[1]
	16.5	162					[2]
	16	274					[21]
$1^2\Delta_u$	Repulsive						Present work
	Repulsive						[1]
	Repulsive						[2]
$2^2\Delta_g$	28.79	1189	32859	9.38	0.019	0.0037	Present work
	30.65	698	33174	7.83	0.01	0.003278	[1]
	28.75	1174					[2]
$2^2\Delta_u$	53.50	67	33968	3.58	0.047	0.0011	Present work
	55.82	40	33832	1.77	0.01	0.000988	[1]
	Repulsive						[2]

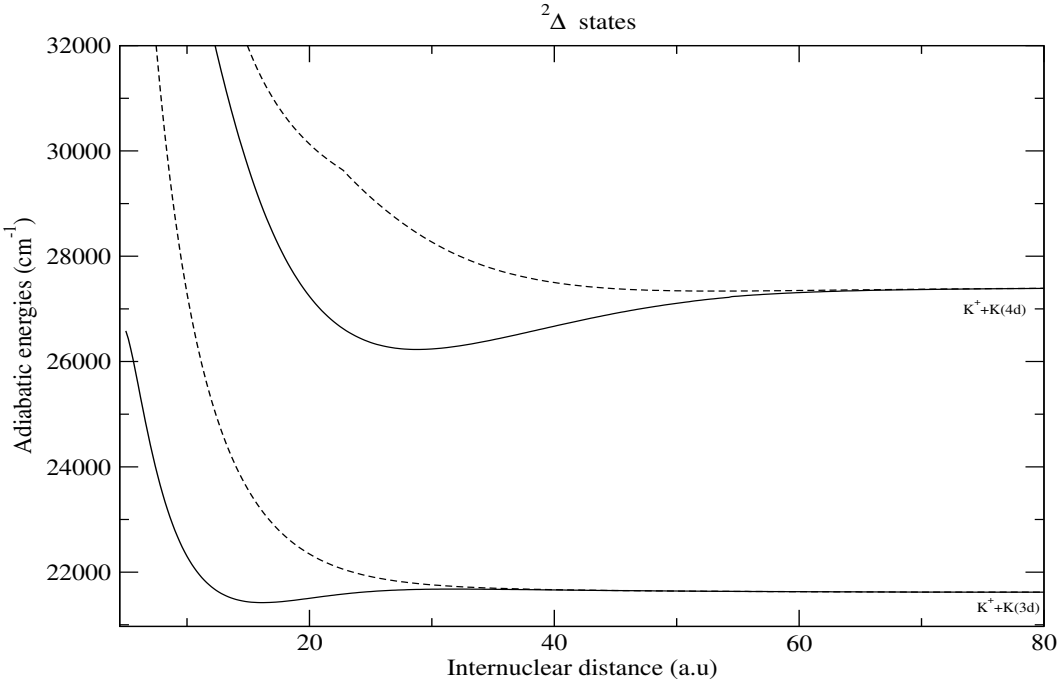

Figure 4: K_2^+ potential energy curves given with respect to the ground state dissociation limit. Δ_g in solid line, Δ_u in dashed lines.

4. Avoided crossings

The obtained potential energy curves exhibit several avoided crossings between adjacent adiabatic states which belong to the same molecular symmetry. In Table 6, we give the internuclear distance R_c of the pseudo-crossing and the corresponding energy gap ΔE_c. Such quantities are required to evaluate cross sections of charge transfer process when Landau-Zener [30] approximation is used. Except the avoided crossing $2^2\Pi_g - 4^2\Pi_g$, our internuclear distances R_c of the pseudo-crossing compare favourably to the ones issued from an ab-initio approach [1].

Table 6: Avoided crossing parameters R_c and ΔE_c

Crossing	$R_c(a.u)$	$\Delta E_c(a.u)$	Reference
$2^2\Sigma_g^+ - 3^2\Sigma_g^+$	5.71	5.57 10^{-3}	Present work
	5.65		[1]
$3^2\Sigma_g^+ - 4^2\Sigma_g^+$	18.28	1.74 10^{-3}	Present work
	18.19		[1]
$5^2\Sigma_g^+ - 6^2\Sigma_g^+$	10.28	1.16 10^{-2}	Present work
	10.38		[1]
$6^2\Sigma_g^+ - 7^2\Sigma_g^+$	43.02	5.05 10^{-3}	Present work
	40.91		[1]
$3^2\Sigma_u^+ - 4^2\Sigma_u^+$	29.58	1.79 10^{-3}	Present work
	30.07		[1]
$2^2\Pi_g - 4^2\Pi_g$	9.90	1.99 10^{-2}	Present work
	6.74		[1]

5. Conclusion

We have investigated the K_2^+ alkali-dimer using a model potential approach to compute the adiabatic potential energies and the molecular spectroscopic constants for the first low-lying states (fourteen $^2\Sigma^+$, eight $^2\Pi$ and four $^2\Delta$), dissociating up to the K^++K(6s) limit.

Present results compare well to those based on *ab initio* [1] methods, which is a clear indication that model potential approach remains an efficient way of providing an accurate description of molecular systems involving a single active electron.

On the other hand, it is interesting to underline that previous existing disagreement between *ab-initio* results [1] and those based on a model potential approach [2], concerning the 5 $^2\Sigma_u^+$, $6^2\Sigma_g^+$, $6^2\Sigma_u^+$, $7^2\Sigma_g^+$, $7^2\Sigma_u^+$, $3^2\Pi_g$, $4^2\Pi_g$ and $2^2\Delta_u$ 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 states are attractive with a well pronounced energy minimum. This is in a perfect agreement with results predicted by studies exploiting *ab-initio* techniques.

6. References

[1] H. Berriche, C. Ghanmi, M. Farjallah, H. Bouzouita, J. Comp. Meth. Sci. and Eng. 8 (2008) 297.
[2] S. Magnier, M. Aubert-Frécon, J. Quant. Spectro. and Rad. Trans. 78 (2003) 217.
[3] P. Siegbahn, B. Liu, J. Chem. Phys. 68 (1978) 2457.
[4] H. Partridge, D. W. Schwenke, J. Chem. Phys. 106 (1997) 4618.
[5] F. Bernardi, M. Olivucci, M. A. Robb, Chem. Soc. Rev. 25 (1996) 321.
[6] S. Sato, J. Chem. Phys. 23 (1955) 592.
[7] M. Born, R. Oppenheimer, Ann. Phys. 84 (1927) 457.
[8] I. Schmidt-Mink, W. Müller, W. Meyer, Chem. Phys. 92 (1985) 263.
[9] L. Von Szentpaly, P. Fuentealba, H. Preuss, H. Stoll, Chem. Phys. Lett. 93 (1982) 555.
[10] S. Magnier, S. Rousseau, A. R. Allouche, G. Hadinger, Aubert-Frécon, Chem. Phys. 246 (1999) 57.
[11] P. Jasik, J. Wilczyński, J.E. Sienkiewicz, Eur. Phys. J. 144 (2007) 85.
[12] W.C. Stwalley, H. Wang, J. Mol. Spect. 195 (1999) 194.
[13] S. Leutwyler, M. Hofmann, H.P. Harri, E. Schumacher, Chem. Phys. Lett. 77 (1981) 257.
[14] M. Broyer, J. Chevaleyre, G. Delacretaz, S. Martin, L. Wöste, Chem. Phys. Lett. 99 (1983) 206.
[15] D.D. Konowalow, M.E. Rosenkrantz, Electronic structure and spectra of light alkali diatomic molecules and their molecular cations, in: J.L. Gole, W.C. Stwalley (Eds.), Metal Bonding and Interactions in High Temperature Systems with Emphasis on Alkali Metals, Am. Chem. Soc. Symp. Ser. 179 (1982) 3.
[16] E. Ilyabaev, U. Kaldor, J. Chem. Phys. 98 (1993) 7126.
[17] A. Valance, J. Chem. Phys. 69 (1978) 355.
[18] P. Skupin, M. Musial, S.A. Kucharski, J. Phys. Chem. A. 121 (2017) 1480.
[19] A. Jraij, A.R. Allouche, S. Magnier, M. Aubert-Frécon, Can. J. Phys. 86 (2008) 1409.
[20] A.Henriet, F.Masnou-Seeuws, Chem. Phys. Lett, 101 (1983) 535.
[21] A. Henriet, J. Phys. B.: At. Mol. Phys. 18 (1985) 3085.
[22] M. Klapisch, Comput. Phys. Commun. 2 (1971) 239.
[23] D. Rabli, R. McCarroll, Chem. Phys. 487 (2017) 23.
[24] D. Rabli, R. McCarroll, Chem. Phys. 511 (2018) 63.
[25] W. Müller, W. Meyer W, J. Chem. Phys. 80 (1984) 3311.
[26] Baskkin S, Stoner JO. Atomic energy levels and Grotrian diagrams, vol. 1. Amsterdam: North-Holland, 1978.
[27] S. Magnier, Ph. Millié, Phys. Rev. A. 54 (1996) 204.
[28] A. Kramida, Y. Ralchenko, J. Reader and NIST ASD Team (2018). NIST Atomic Spectra Database (ver. 5.6.1).
[29] P. Fuentealba, H. Preuss, H. Stoll, L. Von Szentpaly, Chem. Phys. Lett. 89 (1982) 418.
[30] C. Zener, Proc. R. Soc. London. 137 (1932) 696.
[31] R. McCarroll and P. Valiron, Astronomy and Astrophysics, 53, (1976) 83.
[32] R. McCarroll and P. Valiron, Astronomy and Astrophysics, 53, (1978) 177.
[33] M. Philippe, F. Masnou-Seeuws, P. Valiron, J. Phys. B: At. Mol. Phys. 12, No. 15, 1979
[34] P. Valiron, R Gayet, R McCarroll, F Masnou-Seeuws, M. Philippe J. Phys. B: At. Mol. Phys. 12 (1979) 53.
[35] F. Masnou-Seeuws, M. Philippe, P. Valiron, Phys. Rev. Lett. 41, (1978) 395.