



HAL
open science

The low-lying adiabatic states of the $K + 2$ alkali dimer

Djamal Rabli, Ronald Mccarroll

► **To cite this version:**

Djamal Rabli, Ronald Mccarroll. The low-lying adiabatic states of the $K + 2$ alkali dimer. Chemical Physics Letters, 2019, 723, pp.82-88. 10.1016/j.cplett.2019.02.051 . hal-02169263

HAL Id: hal-02169263

<https://hal.sorbonne-universite.fr/hal-02169263v1>

Submitted on 1 Jul 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Djamal Rabli¹, Ronald McCarroll¹

*Sorbonne Université, UMR 7614 du CNRS,
Laboratoire de Chimie Physique-Matière et Rayonnement, 75231-Paris Cedex 05, France*

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]. Moreover, 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

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

[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, $\omega_e=73.40\text{ cm}^{-1}$ and $\omega_e\chi_e=0.2\text{ cm}^{-1}$, respectively.

From the theoretical point of view, multi-electron *ab-initio* calculations have been performed by Konowalow and Rosenrants [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 Jraj *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 Henriët and Masnou-seeuws [20] to generate the spectroscopic constants of the ground state. In an alternative study also based on model potential approach, Henriët [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] |
|-----------------------------|--------------|----------|----------|----------|
| $\text{K}^+ + \text{K}(4s)$ | 0.00 | 0.00 | 0.00 | 0.00 |
| $\text{K}^+ + \text{K}(4p)$ | 13092.54 | 13077.61 | 13022.99 | 13042.90 |
| $\text{K}^+ + \text{K}(5s)$ | 21010.53 | 20980.67 | 21018.02 | 21026.55 |
| $\text{K}^+ + \text{K}(3d)$ | 21665.98 | 21575.01 | 21535.54 | 21536.99 |
| $\text{K}^+ + \text{K}(5p)$ | 24712.41 | 24670.70 | 24750.85 | 24720.14 |
| $\text{K}^+ + \text{K}(4d)$ | 27438.61 | 27366.94 | 27417.26 | 27398.15 |
| $\text{K}^+ + \text{K}(6s)$ | 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 $\text{K}^+ + \text{K}(6s)$ 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 $\text{K}^+(3p^6)$ is described by a model potential proposed by Klapisch [22] which has been used in a previous work by Magnier and Frécon [2]:

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

where r denotes the radial distance of the electron from 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

$$H_{\text{model}} = T + V_{\text{model}}, \quad (2)$$

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).

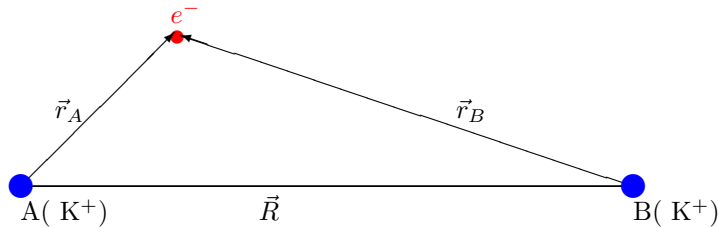


Figure 1: Relative coordinates for the active electron.

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 K₂⁺ molecular cation is then treated as a set of two closed shell K⁺(3p⁶) cores and a single active electron moving in the field created by the two ionic cores. The electronic Hamiltonian is given by

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

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:

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

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

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

is the azimuthal angle.

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

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

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 $\Lambda = |m| = 0, 1, 2, \dots$ for Σ^+ , Π and Δ molecular states respectively.

3. Results

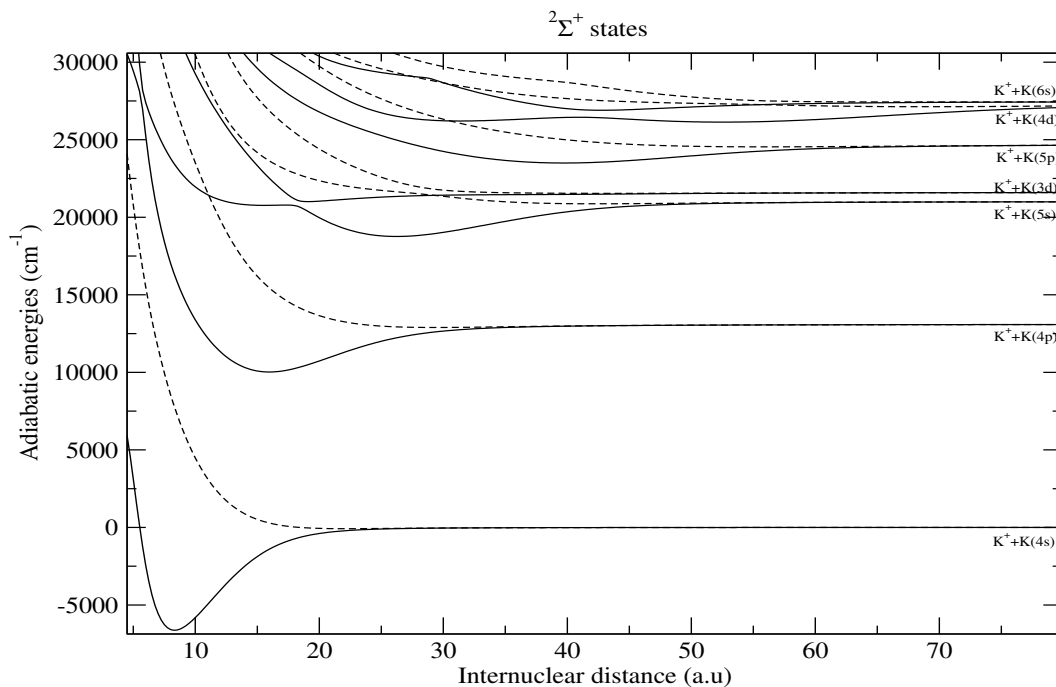


Figure 2: K_2^+ potential energy curves given with respect to the ground state dissociation limit. Σ_g^+ in solid lines, Σ_u^+ in dashed lines.

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 | | | | | | |
| $7^2\Sigma_u^+$ | 67.74 | 26 | 34064 | 1.32 | 0.017 | 0.0007 | Present work |
| | 70.27 | 19 | 33895 | 1 | 0.04 | 0.000623 | [1] |
| | Repulsive | | | | | | |

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 $D_e = 6630 \text{ cm}^{-1}$, an equilibrium distance $R_e = 8.33 \text{ a.u.}$, vibration constants $\omega_e = 73.04 \text{ cm}^{-1}$ and $\omega_e\chi_e = 0.201 \text{ cm}^{-1}$. Those values may be compared to the *ab-initio* results [1], $D_e = 6454 \text{ cm}^{-1}$, $R_e = 8.58 \text{ a.u.}$, $\omega_e = 73.05 \text{ cm}^{-1}$ and $\omega_e\chi_e = 0.14 \text{ cm}^{-1}$. On the other hand, as indicated in Table 3, it is interesting to note that our dissociation energy compares well to the experimental value $D_e = 6670 \text{ cm}^{-1}$, 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 $R_e = 22.18 \text{ a.u.}$, with a corresponding dissociation energy $D_e = 80 \text{ cm}^{-1}$. As shown in Table 3, these values compare well to the ones issued from different approaches [1, 2, 18]. Our vibration constants $\omega_e = 5.72 \text{ cm}^{-1}$ and $\omega_e\chi_e = 0.102 \text{ cm}^{-1}$ are in perfect agreement with those based on *ab-initio* method [1], $\omega_e = 5.72 \text{ cm}^{-1}$ and $\omega_e\chi_e = 0.13 \text{ cm}^{-1}$.

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 $D_e = 3070 \text{ cm}^{-1}$ and an internuclear equilibrium distance $R_e = 15.96 \text{ a.u.}$ These values may be compared to the *ab-initio* ones [1], $D_e = 3038 \text{ cm}^{-1}$, $R_e = 16.02 \text{ a.u.}$ and to the ones resulting from a model potential approach [2], $D_e = 3048 \text{ cm}^{-1}$ and $R_e = 16.00 \text{ a.u.}$

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

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 $\omega_e = 2.91$ cm^{-1} and $\omega_e\chi_e = 0.012$ cm^{-1} compare well to the *ab-initio* results [1], $\omega_e = 3.04$ 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 $\omega_e = 9.56$ cm^{-1} and $\omega_e\chi_e = 0.019$ cm^{-1} . Moreover, 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 initio* 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.

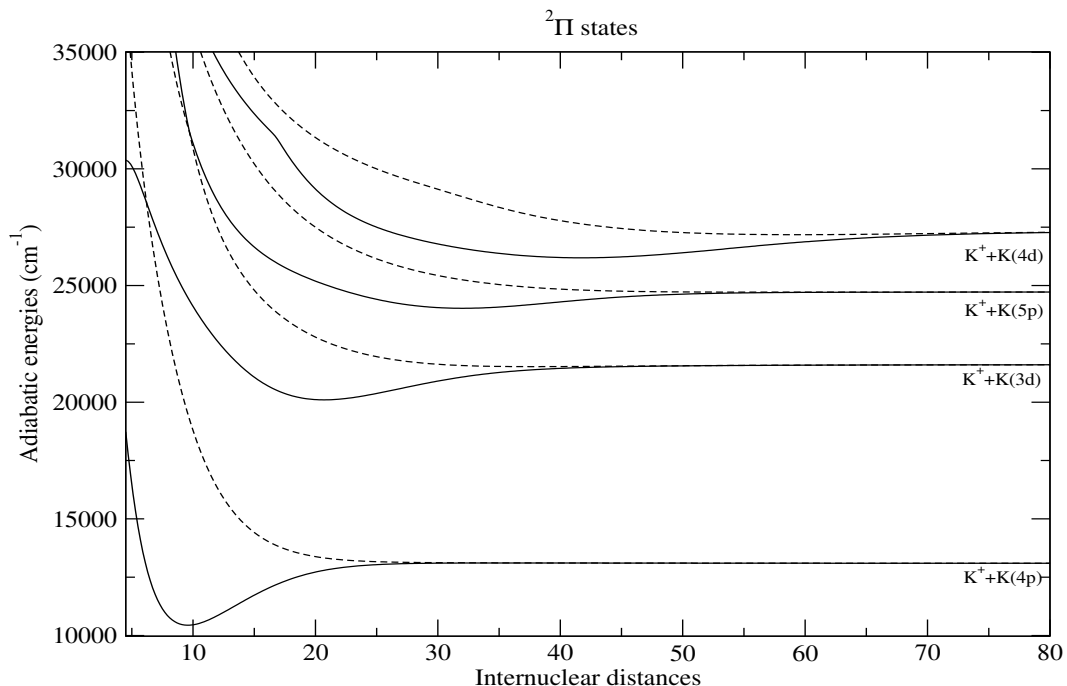


Figure 3: K_2^+ potential energy curves given with respect to the ground state dissociation limit. Π_u in solid lines, Π_g in dashed lines.

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 $\omega_e = 9.42$ cm^{-1} and $\omega_e\chi_e = 0.032$ cm^{-1} , are slightly different from the *ab-initio* values [1], $\omega_e = 8.32$ 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 $\omega_e=6.96$ cm^{-1} and $\omega_e\chi_e=0.010$ cm^{-1} , which compare favorably with the *ab-initio* values [1], $\omega_e=7.4$ 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 Henriot [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 $\text{K}^++\text{K}(4d)$ 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] |

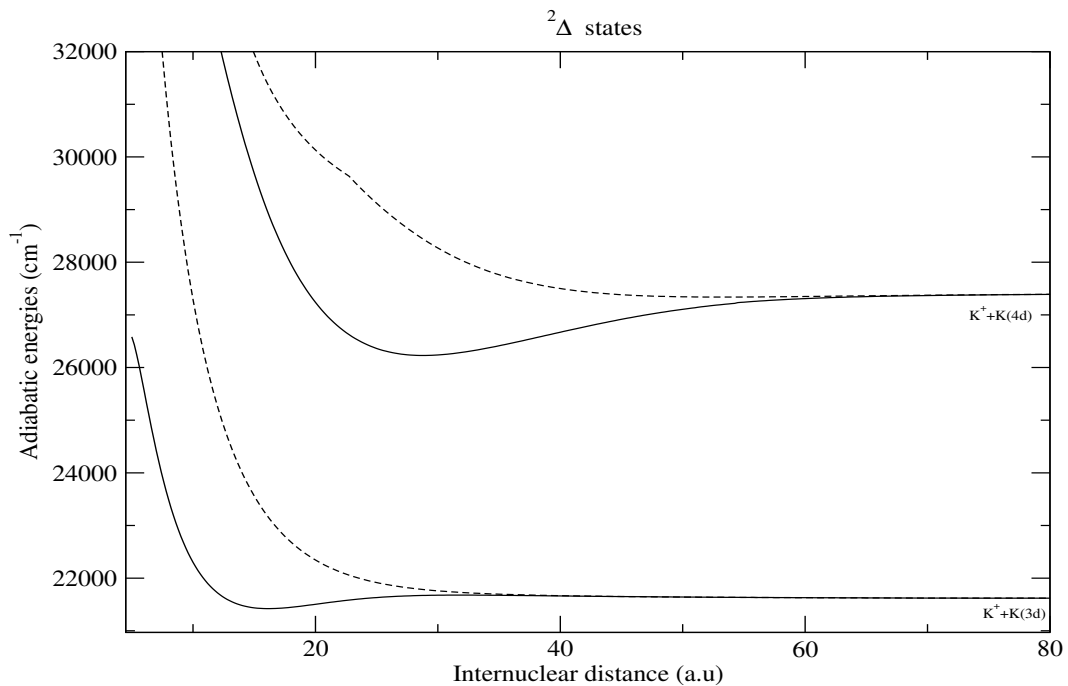


Figure 4: K_2^+ potential energy curves given with respect to the ground state dissociation limit. Δ_g in solid line, Δ_u in dashed lines.

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 | $5.57 \cdot 10^{-3}$ | Present work |
| | 5.65 | | |
| $3^2\Sigma_g^+ - 4^2\Sigma_g^+$ | 18.28 | $1.74 \cdot 10^{-3}$ | Present work |
| | 18.19 | | |
| $5^2\Sigma_g^+ - 6^2\Sigma_g^+$ | 10.28 | $1.16 \cdot 10^{-2}$ | Present work |
| | 10.38 | | |
| $6^2\Sigma_g^+ - 7^2\Sigma_g^+$ | 43.02 | $5.05 \cdot 10^{-3}$ | Present work |
| | 40.91 | | |
| $3^2\Sigma_u^+ - 4^2\Sigma_u^+$ | 29.58 | $1.79 \cdot 10^{-3}$ | Present work |
| | 30.07 | | |
| $2^2\Pi_g - 4^2\Pi_g$ | 9.90 | $1.99 \cdot 10^{-2}$ | Present work |
| | 6.74 | | |

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. Jraj, A.R. Allouche, S. Magnier, M. Aubert-Frécon, Can. J. Phys. 86 (2008) 1409.
- [20] A. Henriët, F. Masnou-Seeuws, Chem. Phys. Lett, 101 (1983) 535.
- [21] A. Henriët, 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.