



Ab initio multi-reference perturbation theory calculations of the ground and low-lying electronic states of the KRb molecule



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ABSTRACT

The potential energy curves of the low-lying electronic states correlating up to the limit $K(4p) + Rb(5s)$ of KRb molecule have been calculated using the multi-reference perturbation theory method at the CASSCF/XMCQDPT2 level of theory without and with spin–orbit coupling. The calculated parameters of the ground $X^1\Sigma^+$ state are in the best agreement among all previously performed *ab initio* calculations for the KRb molecule. The calculated vibrational intervals of the ground electronic term of the $^{39}K^{85}Rb$ molecule describe the experiment with the accuracy within $\pm 1 \text{ cm}^{-1}$. The calculated intensities of the $2^1\Sigma^+$ ($v' = 3, J' = 26$) \rightarrow $X^1\Sigma^+$ ($v'' = 0 \dots 24, J'' = 25, 27$) transitions satisfactory reflect the experimentally observed intensities distribution.

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1. Introduction

The KRb molecule is among the most intensively studied polar alkali diatomics, partially because of its successful usage in production and investigation in cold and ultracold conditions (see for instance [1–4]). Recent efforts are often focused on transferring weakly bound ultracold molecules into their “absolute” ground state X ($v'' = 0, J'' = 0$) by additional optical cycles via excited electronic states. The efficiency of these processes depends rather critically on the proper choice of optical paths, which needs reliable information about the potential energy curves (PECs) of the combining electronic states in wide range of energies and internuclear distances. Since the empirical information based on spectroscopy studies is still insufficient, the analysis of the efficiency of optical paths has to include the data from *ab initio* calculations (see for KRb the recent paper [5]).

The goal of the present paper is to perform *ab initio* calculations of PECs of the ground and several excited electronic states of the KRb molecule corresponding to the first three asymptotic limits of separated atoms and to derive molecular constants, vibrational-rotation energies and Franck–Condon factors. The calculation of the electronic structure of molecular systems, which contain a heavy alkali metals atom, is a non-trivial task that requires taking into account the relativistic effects for the core electrons, the static

and dynamic components of the correlation energy, a large number of excited configurations, etc. The diatomic polar molecule KRb is a typical example of the above-mentioned systems. The electronic states of $^{39}K^{85}Rb$ (the most abundant isotopomer, 67.3%) and others stable isotopomers of the KRb molecule ($^{39}K^{87}Rb$, 26.0%, $^{41}K^{85}Rb$, 4.9%, $^{41}K^{87}Rb$, 1.9%) were studied experimentally in [1–4,6–29] and theoretically in [5,30–44]. The investigation of the ground state $X^1\Sigma^+$ was performed by Ross et al. [6], Amiot and Vergès [9], Stwalley [20], Wang et al. [22] and Pashov et al. [13] by employing high-resolution spectra of laser-induced fluorescence yielding the highly accurate PEC. Regarding the excited states, fragmentary experimental data for the next ($2^1\Sigma^+$) singlet state are available in [4,6]. The Dunham coefficients and RKR potential of the $3^1\Sigma^+$ state can be found in Amiot et al. [8]. Aikawa et al. [26] obtained the parameters of the $3^1\Sigma^+$ state PEC. Molecular constants of the “twin” $1^1\Pi$ and $2^1\Pi$ states have been obtained by Kasahara et al. [7], Amiot et al. [10] and Okada et al. [16]; note that the molecular constants of the $2^1\Pi$ state obtained in [7,10] differ substantially. Low-lying KRb triplet terms have been investigated by Pashov et al. [13] ($1^3\Sigma^+$), Kobayashi et al. [15] ($1^3\Pi$), Amiot [11] ($2^3\Sigma^+$), Lee et al. [12,17], Kim et al. [23] ($3^3\Sigma^+$), Banerjee et al. [14] ($2^3\Sigma^+$, $1^1\Pi$) and Kim et al. [23] ($2^3\Pi$). Highly-excited states of the KRb molecule were studied in [8,12,21,23,25,27,29,43].

Ab initio calculations of the KRb electronic states are traditionally [30–34,40,41,43] performed in the multi-configuration CASSCF/MRCI (Complete Active Space Self-Consistent Field/Multi-

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Reference Configuration Interaction) approximation. Such an approach in the case of a multi-configuration problem allows one considering both static part of correlation energy (at the CASSCF level of theory) and its dynamic component (at the MRCI level of theory). Note that both levels of theory, which are consistently applied here, are based on a variational principle. The common feature of calculations [32,33,41] is the sufficiently successful reproduction of the experimental value of the equilibrium internuclear distance R_e equal to 4.06770 Å [13] of the ground electronic state $X^1\Sigma^+$, namely 4.055 [32], 4.09 [33] and 4.095 Å [41]. At the same time these calculations yield significantly lower values of the ground state dissociation energy D_e , namely 4110 [32], 4113 [33] and 4128.8 cm⁻¹ [41] if compared with the experimental value 4217.815 cm⁻¹ [13]. Meyer and Bohn [40] at the above-mentioned level of theory received $R_e = 4.33$ Å and $D_e = 4039$ cm⁻¹. At the coupled clusters (MRCC) level of theory Meyer and Bohn [40] and Fedorov et al. [44] received significantly lower (4062 cm⁻¹) and higher (4306 cm⁻¹) values of D_e , respectively.

Recently [45] a new approach to the MS-MR-PT (Multi-State Multi-Reference Perturbation Theory) level of theory has been developed, which is called XMCQDPT (Extended Multi-Configuration Quasi-Degenerate Perturbation Theory). This approach allows one to look at the considered problem from an alternative point of view, which is not based on variational principle, but exploits the perturbation theory methods. In particular, the XMCQDPT2 method proposed in [45] is approximately size-consistent for low-lying states in contrast to MRCI and other CI methods, which are not size-consistent.

The main goals of this work are: (i) to calculate the PECs of the ground and some low-lying excited states of the KRb molecule at the multi-reference perturbation level of theory and (ii) basing only on the performed without any fitting *ab initio* PECs calculations, to determine other spectroscopic characteristics of the states (vibrational and vibration-rotational energies, etc.). The main attention is paid to the ground $X^1\Sigma^+$ and first triplet $1^3\Sigma^+$ states of the KRb molecule. The empirical PECs of these states are determined with a high accuracy by Pashov et al. [13]. It allows using these PECs as a kind of benchmark for the *ab initio* calculations at the high level of theory. The quality of the present calculated PECs was tested by comparing the predicted Franck-Condon factors with the relative intensity distribution in the $2^1\Sigma^+ \rightarrow X^1\Sigma^+$ transition measured in Laser Centre, University of Latvia.

2. Computations

The small core Stuttgart RSC ECP [46] has been used in our calculations. The Gaussian basis sets used are (11s11p5d3f) → [8s8p5d3f] (ECP10MDF) for the potassium atom and (13s10p5d3f) → [8s7p5d3f] (ECP28MDF) for the rubidium atom [46].

First, the CASSCF calculations with the state-averaged (SA) procedure were done. The active space for the CASSCF calculations was 2 electrons in 14 orbitals. The SA procedure was realized for singlet and triplet states. The SA-CASSCF(2,14) calculations were performed pointwisely with the step of 0.01 Å in the range of interatomic distances from 3.00 to 6.00 Å. In contrast to the automatic PEC scanning, which is less time consuming, but often leads to a divergence of solution at a large distance from the starting point, the point-by-point calculations allow to get the convergence of the solution at the CASSCF level of theory at each point under consideration, as well as to avoid “jumps” of energy and PEC’s breaks. A lack of convergence at using the automatic PEC’s scanning can lead to the errors in the calculations of PEC’s shape [41] (see below). Outside the specified range (2.50–3.00, 6.00–15.00 and 15.00–20.00 Å) the calculations were performed with the steps of

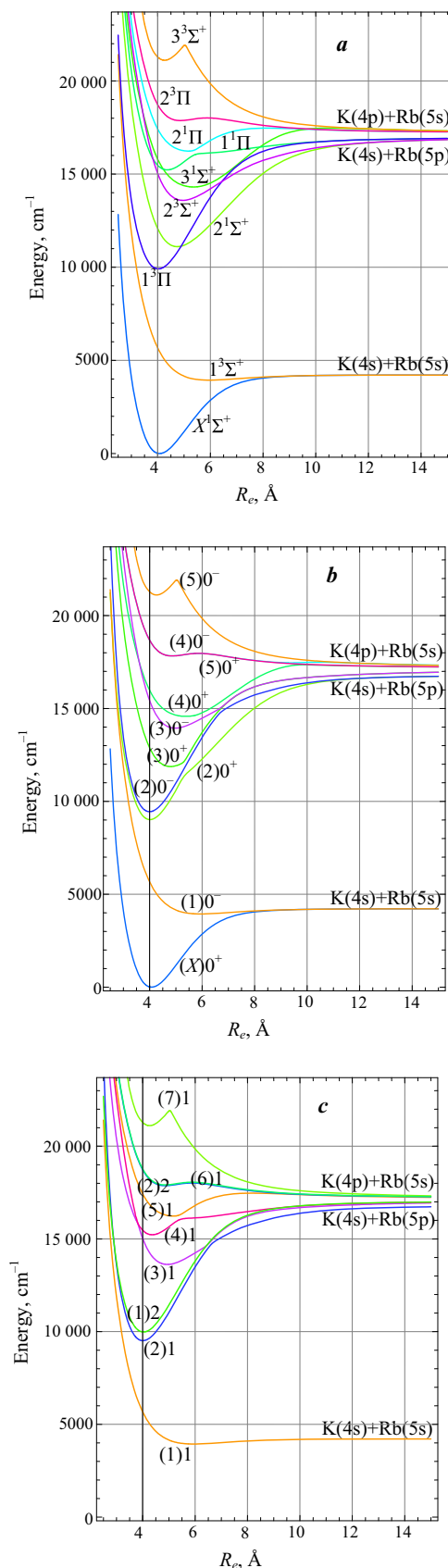


Fig. 1. Calculated at the CASSCF(2,14)/XMCQDPT2 level of theory low-lying singlet and triplet (a) and spin-mixed with $\Omega = 0^+$, 0^- (b) and $\Omega = 1, 2$ (c) terms of the KRb molecule.

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