Journal of Quantitative Spectroscopy & Radiative Transfer 129 (2013) 8–14

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

The effect of inner-shell electrons on the ground and low-lying excited states of KLi: *Ab initio* study with all-electron basis sets

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ARTICLE INFO

Article history:
Received 9 January 2013
Received in revised form
24 May 2013
Accepted 25 May 2013
Available online 4 June 2013

Keywords:
Potential energy curves
Inner-shell electron
All-electron basis sets
Spectroscopic parameters
Analytical potential energy functions

ABSTRACT

The potential energy curves (PECs) have been calculated for the $X^1\Sigma^+$, $A^1\Sigma^+$, $1^3\Sigma^+$, $2^3\Sigma^+$ states of KLi using multireference configuration interaction method and large all-electron basis sets. The calculations take into account the effect of inner-shell electrons with different active spaces. The rotational and vibrational energy levels are obtained by solving the Schrödinger equation of nuclear motion based on the PECs. The spectroscopic parameters are determined from the rotational and vibrational levels and compared with the theoretical and experimental reports in the literature. The PECs are fitted into analytical potential energy functions using the Morse long-range potential function. The effect of inner-shell electrons on the PECs, rotational and vibrational energy levels and spectroscopic parameters is analyzed.

1. Introduction

In the last decade the interest in KLi has been greatly stimulated by the cold physics community. Investigations including the experimental and theoretical effort have been devoted to determination of the potential energy curves (PECs) and spectroscopic constants of KLi molecule. Concerning the experimental investigations, Bednarska et al. [1] obtained rotational constants for the $v=0$ levels of the $X^1\Sigma^+$ state and the $B^1\Pi$ state of KLi by Doppler-free polarization spectroscopy in 1996. They [2] also reported the molecular constants for the $v''=0$–3 levels of the $X^1\Sigma^+$ state and $v'=0$–3 levels of the $B^1\Pi$ state of KLi. In 1998, Jastrzebski et al. [3] measured the Doppler-free polarization spectrum for the $B^1\Pi$–$X^1\Sigma^+$ band system using the same method and reported the Dunham coefficients for the X state and *f*-parity levels of the B state. In the same year, Bednarska et al. [4] studied the ground state $X^1\Sigma^+$ of KLi by analyzing spectra of the $B^1\Pi$–$X^1\Sigma^+$ system and obtained the rotational and vibrational constants for $X^1\Sigma^+$ state. Pashov et al. [5] derived accurate molecular constants for the B and C states using Dunham expansion. Martin et al. [6] observed 47 vibrational levels of the electronic ground state for KLi by laser-induced fluorescence spectra of the B–X system recorded on a Fourier transform interferometer in 2001. Jastrzebski et al. [7] studied the $B^1\Pi$ and $C^1\Sigma^+$ states for KLi using the polarization labeling spectroscopy method. Grochola et al. [8,9] derived the molecular constants and PECs of the $D^1\Pi$ state and observed the $4^1\Pi$– $X^1\Sigma^+$ band system of KLi by the same experimental method as Jastrzeski et al. [7]. In 2007, Salami et al. [10] constructed PECs for the $a^3\Sigma^+$ state of KLi from a limited vibrational data set. In 2008, Jedrzejewski et al. [11] reported $6^1\Pi$–$X^1\Sigma^+$ and $7^1\Pi$–$X^1\Sigma^+$ band systems. Tiemann et al. [12] studied the two lowest states $a^3\Sigma^+$ and $X^1\Sigma^+$ predicting positions of Feshbach resonances and observing corrections to the Born-Oppenheimer approximation in 2009. Szczepkowski et al. [13] analyzed the spectra simplified by polarization labeling and constructed the exotic molecular potential of the $4^1\Sigma^+$ state of KLi in 2010. Grochola et al. [14] investigated the $A^1\Sigma^+$–$X^1\Sigma^+$ band system by the same method as that of Jastrzebski et al. [7].

On the theoretical side, Müller and Meyer [15] studied the KLi molecule via pseudo-potential calculations for the

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http://dx.doi.org/10.1016/j.jqsrt.2013.05.025

first time and obtained the spectroscopic constants for the ground state and the lower excited states. In 1999, Rousseau et al. [16] made a non-empirical one-electron pseudopotential, polarization potential and full-valence configuration interaction calculations for 58 electronic states of $^{1,3}\Sigma^{+}$, $^{1,3}\Pi$ and $^{1,3}\Delta$ symmetries. In 2012, Dardouri et al. [17] made a study of 48 electronic states of KLi molecule relying on an *ab initio* pseudo-potential calculation. The calculations were performed using the empirical pseudo-potential to describe the effect of inner-shell electrons. Therefore, the effect of inner-shell electrons on the PECs and spectroscopic properties is not understood clearly although their calculational results correspond to the experimental values well. In the present work we performed systematical calculations for these states in different active spaces and all-electron basis sets are used to examine effect of inner-shell electrons more completely. Based on the dense potential energy points, the analytical potential energy function (APEF) is fitted employing the Morse long-range (MLR) potential energy function suggested by Le Roy [18,19]. Next the energies of rovibrational levels of KLi are calculated by solving the radial Schrödinger equation of nuclear motion and then the spectroscopic parameters are fitted to the rotational and vibrational levels with Dunham series expansion for the term values, the results compared with previous theoretical and experimental works.

2. Theoretical details

The multireference configuration interaction (MRCI) [20,21] procedure is believed to be a high-quality *ab initio* quantum chemical method in treating the electron correlation. Combined with suitable basis sets it can give convincing data of the PEC for KLi. In this work the MRCI method and the large all-electron basis sets def2-AQZVPP-JKFI for K, aug-cc-pCV5Z for Li have been used. All calculations are performed using MOLPRO package [22]. To examine various effects of the inner-shell and valence electrons, we perform PECs of the considered states with different active spaces used for calculations. The first one is complete valence electron space of KLi. In fact, the active space consists of $4s^24p^6$ of K and $2s^22p^6$ of Li (hereafter called AS1), and contains only two electrons, *i.e.* $4s^1$ of K and $2s^1$ of Li. The inner-shell considered in the present work is focused on K atom. In the second approach active space includes $3p^64s^24p^6$ of K (AS2), and in the third one it includes $3s^23p^64s^24p^6$ of K (AS3). The MRCI calculations for the two low-lying excited states $1^3\Sigma^+$, $2^3\Sigma^+$ are performed using the same orbitals as for the ground state in order to determine accurately the spectroscopic terms. The PECs are separately calculated in the range of internuclear distances from 2.00 to 21.95 Å for $X^1\Sigma^+$, $A^1\Sigma^+$, $1^3\Sigma^+$, $2^3\Sigma^+$ states with a step of 0.05 Å. APEFs are represented by the Morse long-range potential function suggested by Le Roy [18,19] which was fitted to *ab initio* PECs. Next the rotational and vibrational energy levels of KLi are calculated by solving the radial Schrödinger equation of nuclear motion using LEVEL program package [21], and then the spectroscopic parameters are fitted with Dunham series expansion basing on the rotational and vibrational energy levels. The expression for the rotational and vibrational energy level is

$$E(v,J)=G(v)+E_v(J) \tag{1}$$

where the vibrational energy level $G(v)$ and the rotational sublevel $E_v(N)$ are

$$G(v)=\omega_e(v+1/2)-\omega_e\chi_e(v+1/2)^2+\omega_e y_e(v+1/2)^3 +\omega_e z_e(v+1/2)^4 \tag{2}$$

$$E_v(J)=B_vJ(J+1)-D_vJ^2(J+1)^2+H_vJ^3(J+1)^3 \tag{3}$$

ω_e is the harmonic frequency, $\omega_e x_e$, $\omega_e y_e$, $\omega_e z_e$ are the constants related to anharmonicity of the potential.

The centrifugal distortion constants B_v, D_v are defined by

$$B_v=B_e-\alpha_e(v+1/2)+\gamma_e(v+1/2)^2 \tag{4}$$

$$D_v=D_{rot}+\beta_e(v+1/2) \tag{5}$$

v and J are the vibrational quantum number and rotational quantum number, respectively. B_e, α_e, γ_e, D_{rot}, β_e are rotational constants.

We represented the term values $T(v,J)$ by the Dunham expansion

$$T(v,J)=\sum_{m,n}Y_{mn}(v+1/2)^m[J(J+1)]^n \tag{6}$$

The Dunham coefficients Y_{mn} were calculated using a least-square fitting procedure and they are related to more familiar spectroscopic constants

$$Y_{10}\approx\omega_e,\quad Y_{20}\approx-\omega_e\chi_e,\quad Y_{30}\approx\omega_e y_e,\quad Y_{40}\approx\omega_e z_e,\quad Y_{01}\approx B_e,\quad Y_{11}\approx-\alpha_e,\quad Y_{21}\approx\gamma_e,\quad Y_{02}\approx-D_{rot},\quad Y_{12}\approx-\beta_e \tag{7}$$

It is necessary to point out that R_e and D_e are obtained from the APEFs, but the other spectroscopic parameters result from fits to the rotational and vibrational levels with Dunham series expansion for the term values.

Furthermore, to describe quantitatively the quality of the fitting process, the Root Means Square (RMS) error is calculated with

$$\text{RMS}=\frac{1}{N}\sqrt{\sum_{i=1}^{N}(V_{APEF}-V_{ab\ intio})^2} \tag{8}$$

where V_{APEF} and $V_{ab\ initio}$ are energies given by the fitted and *ab initio* calculations, respectively. N is the number of points, $N=400$ corresponds to number of points for PECs calculations.

3. The expression of APEF

Morse long-range potential function suggested by Le Roy [18,19] seems to have an advantage comparing to other functions proposed to fit APEF of diatomic molecules when the long-range behavior of PEC is considered. So we now choose it to describe KLi molecule. The general MLR function is

$$V_{MLR}(R)=D_e\left\{1-\frac{u_{LR}(R)}{u_{LR}(R_e)}e^{-\Phi_{MLR}(R)Y_p(R)}\right\} \tag{9}$$

where D_e is the dissociation energy, R and R_e are the interatomic distance and the equilibrium bond length,