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Quasi-relativistic treatment of the low-lying KCs states

J.T. Kim [a], Y. Lee [b], A.V. Stolyarov [c,*]

[a] Department of Photonic Engineering, Chosun University, Gwangju 501-759, South Korea
[b] Advanced Photonics Research Institute, Gwangju Institute of Science and Technology, Gwangju 500-712, South Korea
[c] Department of Chemistry, Moscow State University, Leninskie gory 1/3, Moscow 119991, Russia

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ABSTRACT

The potential energy curves, permanent and transition dipole moments as well as spin-orbit and angular coupling matrix elements between the KCs electronic states converging to the lowest three dissociation limits were evaluated in the basis of the spin-averaged wavefunctions corresponding to pure Hund's coupling case (**a**). The quasi-relativistic matrix elements have been obtained for a wide range of internuclear distance by using of small (9-electrons) effective core pseudopotentials of both atoms. The core-valence correlation has been accounted for a large scale multi-reference configuration interaction method combined with semi-empirical core polarization potentials. The static dipole polarizabilities of the ground $X^1\Sigma^+$ and $a^3\Sigma^+$ states were extracted from the closed-shell coupled-cluster energies by the finite-field method. Among the singlet and triplet Σ^+ states manifold the pronounced avoided crossing effect between repulsive walls of the $(2,3)^3\Sigma^+$ states has been discovered and analyzed by finite-difference calculation of radial coupling matrix elements. The resulting transition dipole moments and potentials were used to predict radiative lifetimes and emission branching ratios of excited vibronic states while the calculated angular coupling matrix elements were transformed to Λ-doubling constants of the $(1,2)^1\Pi$ states and magnetic *g*-factor of the ground state. The accuracies of the present results are discussed by comparing with experimental data and preceding calculations.

1. Introduction

Recent progress in cold molecule formation of the mixed alkali dimers such as KRb [1], RbCs [2], LiCs [3] by photoassociation (PA) method provides routes for population transfer to the ground $X^1\Sigma^+$ state and highly anisotropic electric dipole–dipole forces give access to quantitatively new regimes unavailable previously to ultracold homonuclear systems. In particular, nonzero electronic permanent dipole moment d (EPDM) of heteronuclear molecules interacting strongly with inhomogeneous electric field might be used as qubit prototype of a scalable quantum computer [4]. Also, control of ultracold chemical reactions has been proposed by using weakly bound, electric field-linked states of participating molecules [5]. Large anisotropic polarizability α of polar molecules strongly enhances fundamental parity-violation effects caused by electric permanent dipole moment of the electron [6] since long coherence times associated with ultracold temperatures can lead to dramatically increased sensitivity in measurements of these effects. The EPDM and space components of static dipole polarizabilities also provide unique fundamental information about the electronic density changing on adiabatic surfaces.

So far there is poor experimental information about KCs molecule compared to other alkali polar diatomics. Indeed, a highly accurate adiabatic potential energy curve (PEC) $U_X^{IPA}(R)$ for the ground $X^1\Sigma^+$ state of KCs has been constructed for a wide range of internuclear distances R using the high resolution Fourier transform analysis of laser induced fluorescence spectra [7] while average static (dc) electric dipole polarizability of the ground state $\bar{\alpha}_X$ has been measured using molecular beam deflection in an inhomogeneous electric field [8]. Preliminary spectral information about PECs for the lowest triplet $a^3\Sigma^+$ state [7] as well as strongly mutually perturbed $2^1\Sigma^+$ and $1^3\Pi$ excited states became available quite recently [9].

Theoretical data of KCs molecule are not comprehensive one as well. The adiabatic PEC $U_X^{ab}(R)$ and EPDM $d_X^{ab}(R)$ of the $X^1\Sigma^+$ state have been obtained near equilibrium distance R_e in the framework of pseudopotential configuration interaction calculations using large basis set [10]. Non-relativistic *ab initio* large core (1-electron) pseudopotential full-valence configuration interaction calculations combined with the *l*-dependent core polarization potential have been performed for ground and excited electronic states [11–13]. As a result, the adiabatic PECs $U_i^{ab}(R)$, EPDMs $d_i^{ab}(R)$ and electric transition dipole moments (ETDMs) $d_{ij}^{ab}(R)$ for the low-lying

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* Corresponding author. Fax: +7 495 939 02 83.
E-mail addresses: kimjt@chosun.ac.kr (J.T. Kim), avstol@phys.chem.msu.ru, avstol@gmail.com (A.V. Stolyarov).

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excited states corresponding to pure Hund's coupling case (**a**) were obtained for a wide R-range. The same computational procedure for energy was combined with finite-field method in Ref. [14] in order to estimate parallel $\alpha_i^{\parallel}(R)$ and perpendicular $\alpha_i^{\perp}(R)$ components of static dipole polarizability of the $X^1\Sigma^+$ and $a^3\Sigma^+$ states. The spin-orbit coupling (SOC) effect on the non-relativistic PECs have been considered only in Ref. [15] through a semiempirical SO pseudopotential added to the electrostatic Hamiltonian.

There is still no PA experiment for KCs molecule while it is challenging to perform comprehensive PA study of the excited KCs states due to complicated electronic structure and numerous intramolecular perturbations caused by pronounced SOC effect. Furthermore, accurate energy and dynamic properties of the strongly coupled excited states are required to develop a unified non-adiabatic approach for modeling and optimizing the PA experiments. Recently, the inverted channel coupling approach (ICCA) provided pathways addressing deperturbation problems in RbCs [16], NaRb [17] and NaCs [18]. However, highly accurate spin-orbit $\xi_{ij}^{so}(R)$, radial $B_{ij}(R)$ and angular $L_{ij}^{\pm}(R)$ coupling matrix elements are indispensably needed to make this ambiguous analysis a feasible procedure.

Therefore, main motivation of the present work is to evaluate explicitly the required non-adiabatic coupling matrix elements between the ten lowest electronic states of KCs molecule in a wide range of internuclear distance by means of both shape and energy consistent small core (9-electrons) effective core potentials combined with alternative methods accounting for electronic correlation in order to test the reliability of the present and preceding quasi-relativistic calculations. Furthermore, the calculated ETDMs and PECs are used to predict radiative lifetimes and emission branching ratios of excited vibronic states. These dynamic properties could be useful, for example, for the decay rate estimates of the states involved in optical cycles to produce ultra cold ground state molecules by PA method [3].

2. Computational details

The inner core shells of the potassium K and cesium Cs atoms were replaced by spin-orbit averaged non-empirical effective core potentials (ECPs), leaving 9 valence electrons (9-ve) of each atom for explicit treatment. Both shape [19,20] (basis-A) and energy (basis-B) [21] consistent basis sets were used in the present quasi-relativistic calculations. The relevant spin-averaged and spin-orbit Gaussian basis sets used for each atom were borrowed from the above references. Shape-consistent ECPs were augmented by diffuse part of the all-electron bases for electric property calculation [22] and extended by additional diffuse and polarization functions [23,24].

The optimized molecular orbitals (MOs) were constructed from the solutions of the state-averaged complete active space self-consistent field (SA-CASSCF) problem for the lowest (1–4)$^{1,3}\Sigma^+$ and (1–3)$^{1,3}\Pi$ electronic states taken with equal weights [25]. The dynamical correlation effects were introduced by internally contracted MRCI method [26] which was applied for only two valence electrons keeping the rest frozen, i.e. in a full valence (2-electrons) CI scheme. The resulting active space consists of 14σ and 10π MOs. The l-independent CPPs of both atoms were employed together with the above small core ECPs to take into account for implicitly the residual core-polarization effects [27]. The corresponding ECP scaling SO basis coefficients and CPP cut-off radii were adjusted for each atom in order to reproduce experimental fine-structure splitting of the lowest excited K(4^2P$_{1/2;3/2}$) and Cs(6^2P$_{1/2;3/2}$) states [28], respectively. All electronic calculations were performed by means of the MOLPRO v.2006.1 program package [29].

Since a systematic error of the resulting electronic energy weakly depends on the vertical energy excitation the residual R-dependent part of error (first of all these are basis set superposition error as well as dispersion and repulsive correction to large core potential estimates) in the original *ab initio* curves $U_i^{ab}(R)$ was diminished for the excited states through the semi-empirical relation [30]:

$$U_i^{dif}(R) = \left[U_i^{ab}(R) - U_X^{ab}(R)\right] + U_X^{IPA}(R) \tag{1}$$

where $U_X^{IPA}(R)$ is the highly accurate empirical IPA PEC available for the ground $X^1\Sigma^+$ state in a wide R-range [7].

The relevant EPDM $d_i(R) = -\langle\Psi_i^{el}|\sum_{j\in K,Cs}Z_j\vec{R}_j - \sum_i e_i\vec{r}_i|\Psi_i^{el}\rangle|_{\vec{\mathbf{r}}}$, ETDM $d_{ij}(R) = \langle\Psi_i^{el}|\sum_i e_i\vec{r}_i|\Psi_j^{el}\rangle|_{\vec{\mathbf{r}}}$, spin-orbit $\xi_{ij}^{so}(R) = \langle\Psi_i^{el}|\sum_i \xi_i\vec{l}_i\vec{s}_i|\Psi_j^{el}\rangle|_{\vec{\mathbf{r}}}$ and angular $L_{ij}^{\pm}(R) = \langle\Psi_i^{el}|\sum_i[l_{ix} \pm il_{iy}]|\Psi_j^{el}\rangle|_{\vec{\mathbf{r}}}$ electronic matrix elements were evaluated in the basis of the zeroth-order (spin-averaged) MRCI wavefunctions $\Psi_i^{el}(\vec{\mathbf{r}};R)$ corresponding to pure Hund's coupling case (**a**) scheme. The positive sign of the resulting EPDM functions indicates the K$^+$Cs$^-$ polarity while a relative sign of the calculated off diagonal ($i{\neq}j$) matrix elements can be arbitrary.

Non-adiabatic radial coupling matrix elements $B_{ij}(R) = \langle\Psi_i^{el}|\partial\Psi_j^{el}/\partial R\rangle|_{\vec{\mathbf{r}}}$ between states of the same spatial and spin symmetry were computed by the central 3-points finite differences for MRCI wavefunctions with the step $h = 5\times10^{-4}$ *au*. Furthermore, the calculated adiabatic PECs $U_{i,j}^a(R)$ for the strongly interacting states were used to estimate their diabatic counterparts $U_{i,j}^d(R)$ in the framework of the simplest two-level approximation [31]:

$$U_{i,j}^a = \left[(U_i^d + U_j^d) \pm \sqrt{(U_j^d - U_i^d)^2 + 4\left|H_{ij}^{el}\right|^2}\right] \Big/ 2 \tag{2}$$

where the electronic coupling matrix element H_{ij}^{el} is assumed to be independent of R. Then, the resulting diabatic PECs were transformed to the radial coupling matrix element $B_{ij}(R)$ according to the simple relation [32]

$$B_{ij}(R) = \frac{\partial \tan^{-1}\left(2H_{ij}^{el}\Big/[U_j^d - U_i^d]\right)}{2\partial R} \tag{3}$$

The origin dependent radial $B_{ij}(R)$ and angular $L_{ij}^{\pm}(R)$ coupling matrix elements were calculated only for the most abundant isotopomer ^{39}K^{133}Cs since for any other isotopomer ρ the required values can be easily recalculated using the relevant $d_{ij}(R)$ and $U_i(R)$ functions [33]:

$$B_{ij}^{\rho} = B_{ij} + \Delta\zeta\Delta U_{ij}d_{ij}; \quad L_{ij}^{\rho} = L_{ij} + R\Delta\zeta\Delta U_{ij}d_{ij} \tag{4}$$

where $\Delta\zeta = \zeta - \zeta^{\rho}$ is the difference of the dimensionless parameters $\zeta = (m_A - m_B)/(m_A + m_B)$ depending only on atomic masses.

At large internuclear distance the calculated *ab initio* ETDM functions $d_{ij}^{ab}(R)$ of the allowed $^1\Pi, ^1\Sigma^+ - X^1\Sigma^+$ and $^3\Pi, ^3\Sigma^+ - a^3\Sigma^+$ transitions have been compared to their asymptotic counterparts [34]:

$$d_{\Sigma-\Sigma}^{LR}(R) = d_{ij}^{A}\left(1 + \frac{2\alpha^B(\omega_A)}{R^3}\right); \quad d_{\Pi-\Sigma}^{LR}(R) = d_{ij}^{A}\left(1 - \frac{\alpha^B(\omega_A)}{R^3}\right) \tag{5}$$

where d_{ij}^A is the relevant dipole transition moment of atom A and

$$\alpha^B(\omega_A) = 2\sum_j \frac{\left(E_j^B - E_0^B\right)\left|d_{0j}^B\right|^2}{\left(E_j^B - E_0^B\right)^2 - \omega_A^2} \tag{6}$$

is the dynamic polarizabilities $\alpha^B(\omega_A)$ of the atom B at the resonance frequencies of atom A. The required atomic transition moments $d_{4P-4S}^{K} = 2.83$, $d_{6P-6S}^{Cs} = 3.23$ *au* were taken from Ref. [35] while the atomic dynamic polarizabilities $\alpha^K(\omega_{Cs}) \approx +1.26\times10^3$, $\alpha^{Cs}(\omega_K) \approx -1.46\times10^3$*au* were evaluated according to the truncated sum (6)