

# Permanent electric dipoles and $\Lambda$ -doubling constants in the lowest $^1\Pi$ states of RbCs

A.Zaitsevskii, E.A.Pazyuk, and A.V.Stolyarov

*Department of Chemistry, Moscow State University, Moscow, 119899, Russia*

O.Docenko, I.Klincare, O.Nikolayeva, M.Auzinsh, M.Tamanis, and R.Ferber

*Department of Physics, University of Latvia, Riga LV-1586*

The article presents first experimental data on the Stark induced  $e - f$  mixing in the  $(4)^1\Pi$  state of the  $^{85}\text{Rb}^{133}\text{Cs}$  molecule, as well as the *ab initio* calculations of permanent electric dipole moments ( $d$ ) in the  $(1, 2, 3, 4)^1\Pi$  states and  $q$ -factors in the  $(2, 4)^1\Pi$  states. Appearance of the “forbidden” lines in the laser induced  $(4)^1\Pi \rightarrow X^1\Sigma^+$  fluorescence spectrum in the presence of electric field allowed us to obtain the ratio  $q/d = 0.9 \times 10^{-7} \text{ cm}^{-1}/\text{D}$  for the rovibronic  $v'(J') = 2(82)$  level of the  $(4)^1\Pi$  state correlating to the  $\text{Rb}(4d) + \text{Cs}(6s)$  atomic limit. Electronic structure calculations on the ground and excited states of the RbCs molecule were performed in the framework of the Hund’s “a” coupling scheme by means of the many-body multipartitioning perturbation theory (MPPT). The *ab initio*  $d(R)$  estimates revealed large values of about  $d \approx -7 \text{ D}$  for the  $(4)^1\Pi$  state. The calculated  $q$  factor value for the  $(2)^1\Pi$  state is in excellent agreement with the literature data. The theoretical estimate of the  $q/d$  ratio for the  $v'(J') = 2(82)$  level of the  $(4)^1\Pi$  state agrees satisfactory well the present experimental value.

## I. INTRODUCTION

The RbCs molecule is considered among convenient species for formation of Bose-Einstein condensate (BEC) and ultra-cold heteronuclear molecules [1] since both cold Rb and Cs atoms can be feasibly prepared by diode lasers. Ultra-cold RbCs molecules have been recently produced in their electronically excited states [2] via photoassociation in ca. 100  $\mu\text{K}$  mixture of  $^{85}\text{Rb}$  and  $^{133}\text{Cs}$  atoms. In particular, Stark effect was registered in the photoassociation experiments [2] allowing to estimate the permanent dipole moment ( $d = 1.3 \text{ D}$ ) of the  $0^+$  state dissociating to  $\text{Rb}(5S_{1/2})$  and  $\text{Cs}(6P_{1/2})$  atoms. The corresponding calculations of the scattering lengths at elastic scattering of cold Rb and Cs atoms have been presented in Ref. [3]. It is also suggested to use Stark effect in polar alkali dimers as the qubits of a quantum computer [4].

First experimental laser spectroscopy data on the ground and excited electronic states of RbCs dimer were obtained [5] by laser induced fluorescence (LIF). High accuracy RbCs ground state molecular constants and IPA potential up to the dissociation limit were derived in Refs.[6–8] by Fourier-transform spectroscopy (FTS). Molecular constants and RKR potentials for the electronically excited  $(2,4,5)^1\Pi$  and  $(3,7)^1\Sigma^+$  states have been obtained by the LIF-FTS method [9]. High resolution resonance enhanced two photon ionization (RE2PI) spectroscopy was applied to study the  $(4)^1\Sigma^+, (3)^1\Pi$  [10] and the  $(5)^1\Sigma^+$  [11] states. An excitation band to the  $(1)^3\Delta$  state was observed by RE2PI method in a cold RbCs beam [12]. The deperturbation analysis of the strongly coupled  $A^1\Sigma^+ \sim b^3\Pi$  complex has been recently performed in Ref.[13]. The adiabatic RbCs potentials have been calculated for 30 lowest  $\Lambda^\pm$  states in the framework

of the Hund’s  $a$ -coupling scheme [14, 15], and later [16] recalculated for 49 lowest  $\Omega^\pm$  states taking into account the spin-orbit interaction through a semi-empirical spin-orbit pseudo-potential.

In the present paper, we report the *ab initio* calculations of permanent electric dipoles in the  $(1\div 4)^1\Pi$  states and  $q$ -factors in the  $(2,4)^1\Pi$  states, respectively, as well as the first experimental observation of the Stark  $e - f$  mixing in the  $(4)^1\Pi$  state of the RbCs molecule. The method has been successfully applied to the  $B, D^1\Pi$  states of NaK [17–19] and NaRb [20] to obtain reliable information about the permanent dipole moments and the  $\Lambda$ -doubling effect. Extra motivation of the current work was to check the possibility of using the Stark effect induced changes in fluorescence polarization for optical imaging of electric field distribution [21].

## II. EXPERIMENT

The diatomic rovibronic  $^1\Pi$  levels with a fixed rotational level  $J'$  possess basically small  $\Lambda$ -splitting  $\Delta_{e/f}$  into two different  $e/f$  parity components which are not interacting with each other in an isolated molecule [22]. In the presence of an external electric field  $E$ , the  $e$  and  $f$  sublevels are mutually mixed via Stark operator. It leads to the appearance of “forbidden” lines in the  $^1\Pi \rightarrow ^1\Sigma^+$  LIF spectrum, in which one can observe the complete  $(P, Q, R)$ -triplet fluorescence series instead of either  $(P, R)$ -doublets or  $Q$ -singlets. One may consider that the intensity of the “forbidden”  $I_f$  lines is borrowed from the “parent”  $I_p$  lines. The observed  $E$ -dependence of the ratio  $I_f/I_p$  for a definite linear polarization of exciting laser beam and excitation/observation directions of LIF radiation allows one [18–20] to obtain the ratio  $|\Delta_{e/f}/d|$ , where  $d$  is the permanent electric dipole moment of a

given rovibronic level  $v'(J')$ .

RbCs molecules were formed from ca. 1:1 mixture of natural Rb (containing 72% of  $^{85}\text{Rb}$  and 28% of  $^{87}\text{Rb}$ ) and Cs metals in a thermal alkali-resistant glass cell at the temperature ca. 570 K. An  $\text{Ar}^+$  laser (Spectra Physics 171) operating in the single mode regime at 501.7 nm wavelength was used to excite the  $(4)^1\Pi \leftarrow X^1\Sigma^+$  transition in RbCs. The subsequent LIF radiation has been dispersed at right angles by a double monochromator with 1200 lines/mm gratings and 5 Å/mm inverse dispersion in first diffraction order, providing, at reasonable slits, the 0.2 Å spectral resolution. Fluorescence was detected in the spectral range 480-490 nm by a FEU-79 photomultiplier operating in photon counting regime. Electric field up to  $E = 2000$  V/cm was applied to 0.6 cm in diameter carefully polished stainless steel Stark disks separated by  $1.5 \pm 0.1$  mm gap.

The fluorescence  $Q$ -progression to the ground state from the particular  $v' = 2, J' = 82$  rovibronic level of the  $(4)^1\Pi$  state of the  $^{85}\text{Rb}^{133}\text{Cs}$  isotopomer was assigned with a help of the experimental data given in Ref.[6]. After choosing the appropriate spectral region which is free of alien fluorescence lines of other origin (Fig. 1), the dc electric field was applied. Polarizers were used to provide a definite linear polarization of LIF and laser excitation, see Fig. 2. The Stark effect in the  $(4)^1\Pi(v' = 2, J' = 82)$  state was detected via appearance of extra (“forbidden”) ( $P, R$ )-lines as demonstrated in Fig. 2. The experimental intensity ratio  $I_f/I_p$  was determined by a Gaussian approximation of the spectral lines profile. The expected  $I_f(E)/I_p(E)$  signals were simulated by using density matrix formalism for the interaction of cw broad band radiation with a diatomic molecule in the presence of external electric field [18, 23]. The Stark energy of  $^1\Pi(J', M')$  magnetic sublevels was calculated accounting for the  $J' \pm \Delta J'$  state mixing. The experimental curve  $I_f(E)/I_p(E)$  was fitted with respect to the single parameter  $|\Delta_{e/f}/d| = 0.61 \times 10^{-3} \text{ cm}^{-1}/\text{D}$ . The value of inverse radiative lifetime of the excited level  $\Gamma = 10^7 \text{ sec}^{-1}$  was used in calculations. It was numerically proven that changes in  $|\Delta_{e/f}/d|$  value do not exceed 1% when  $\Gamma$  varied within an order of magnitude. The uncertainties in the experimental  $I_f/I_p$  values, Stark plates gap and electric field voltage lead to a 20% overall relative error estimate.

### III. CALCULATION

The present electronic structure calculations on the ground and excited states of the RbCs molecule (see Fig. 3) yielding permanent electric dipoles and  $\Lambda$ -doubling estimates were performed at internuclear distances from 6.0 to 14.0 a.u. in the framework of the Hund’s  $a$ -coupling scheme [22] by means of the many-body multipartitioning perturbation theory (MPPT) [24, 25]. In order to incorporate the scalar (spin-independent) relativistic effects into our calculations, we replaced the inner core shells

by the averaged shape-consistent relativistic core pseudopotentials [26, 27], leaving 9 electrons of each atom for explicit treatment. Uncontracted (7s7p5d3f) Gaussian basis sets were obtained by an appropriate extension of those provided in Refs. [26, 27] (see the web page [http://moleq1.chem.msu.ru/qrmb/suppl\\_rbc.html](http://moleq1.chem.msu.ru/qrmb/suppl_rbc.html) for detailed information). Outer-core-like one-particle functions (MOs) were obtained via state-average MC-SCF calculations on the lowest  $^1,3\Sigma$  of RbCs and  $^2\Sigma^+$  of RbCs $^+$  states; during the generation of the remainder MOs the averaging was restricted to the ionic states. The procedure of MPPT correlation treatment employed in the present work was generally similar to that used in Refs.[19, 20]. We constructed and diagonalised the state-selective effective Hamiltonian in the model space spanned by all the possible distributions of two valence electrons among the valence and virtual MOs (full valence CI space); the core-valence correlation and residual core polarization effects were incorporated through perturbative evaluation of effective valence-shell interactions. Spatial electronic angular momentum matrix elements  $L_{\Pi\Sigma}^{ab}(R)$  between the  $^1\Pi$  states under study and the lowest  $^1\Sigma^+$  states were derived from one-particle spin-free transition density matrices computed at the first MPPT order [28]. The evaluation and transformation of the required molecular integrals and CASSCF calculations were performed by means of the COLUMBUS quantum chemistry software [29, 30] while the quasirelativistic MPPT calculations were carried out by the diagrammatic MPPT code DiagPT [25].

The implicit dependence of the permanent dipole moments (PDMS) on the vibrational  $v'$  and rotational  $J'$  quantum numbers was evaluated as the expectation value of the derived *ab initio* functions  $d^{ab}(R)$ :  $d_{vJ}^{\Pi} = \langle v_J^{\Pi} | d^{ab}(R) | v_J^{\Pi} \rangle_R$ , where  $|v_J^{\Pi}\rangle$  are the adiabatic rovibrational wavefunctions for the  $(1 \div 4)^1\Pi$  states treated.

The  $\Lambda$ -splitting for the  $(2, 4)^1\Pi$  states was approximated in the framework of the 2-nd order non-degenerate perturbation theory as  $\Delta_{e/f} = qJ'(J'+1)$  [22], where the so-called  $q$ -factors were represented by the double sums as

$$q_{vJ}^{\Pi} = \frac{1}{2\mu^2} \sum_{\Sigma^+} \sum_{v\Sigma} \frac{|\langle v_J^{\Pi} | L_{\Pi\Sigma}^{ab}(R) / R^2 | v_J^{\Sigma} \rangle_R|^2}{E_{vJ}^{\Pi} - E_{vJ}^{\Sigma}}, \quad (1)$$

where  $\mu$  is the reduced molecular mass while the  $E_{vJ}$  and  $|v_J\rangle$  are the eigenvalues and eigenfunctions of the corresponding adiabatic states. The summation was restricted by the lowest seven and nine  $^1\Sigma^+$  states for the  $2^1\Pi$  and  $4^1\Pi$  state respectively. For both  $^1\Pi$  states, a partial contribution of the two nearest  $^1\Sigma^+$  states, see Fig. 3, was estimated by the direct summation of (1) over the vibrational states  $v_{\Sigma^+}$ . In order to avoid an explicit consideration of the complete eigenvalue and eigenfunction problem for the remote  $^1\Sigma^+$  states, the interaction with the rest  $^1\Sigma^+$  states was accounted by the approximate

sum [31, 32] as

$$q_{vJ}^{\Pi} \approx \frac{1}{2\mu^2} \langle v_J^{\Pi} | R^{-4} \sum_{\Sigma^+} \frac{|L_{\Pi\Sigma}^{ab}(R)|^2}{\Delta U_{\Pi\Sigma}^{ab}(R)} | v_J^{\Pi} \rangle_R, \quad (2)$$

Where  $\Delta U_{\Pi\Sigma}^{ab}(R) = U_{\Pi}^{ab}(R) - U_{\Sigma^+}^{ab}(R)$  is the difference between the corresponding *ab initio* potentials. To minimize the systematic  $R$ -dependent errors (first of all, the basis set superposition errors) in the ordinary *ab initio* curves  $U_i^{ab}$ , the adiabatic difference potentials for all treated excited states were constructed using the relation  $U_i^{dif}(R) = U_i^{ab}(R) + \Delta U_X(R)$ , where  $\Delta U_X(R) = U_X^{IPA}(R) - U_X^{ab}(R)$  is the difference between the highly accurate IPA potential  $U_X^{IPA}$  [8] and the present *ab initio*  $U_X^{ab}$  ground state potentials. The rovibronic energies  $E_{vJ}$  and wavefunctions  $|v_J\rangle$  required for  $d$  and  $q$  calculations were obtained by a numerical solution of the radial Schrödinger equation with the IPA curve for the ground state [8] and the empirical RKR potentials available for the excited  $(2,3,5,7)^1\Sigma^+$  [9, 11, 13] and  $(2,4)^1\Pi$  [9] states. The obtained “difference-based” potentials  $U_i^{dif}$  were used to evaluate the relevant  $E_{vJ}$  values and  $|v_J\rangle$  functions for the rest  $(1,3)^1\Pi$  and  $(4,6,8,9)^1\Sigma^+$  states.

#### IV. RESULTS AND DISCUSSION

The representation of the  $\Lambda$ -splitting as  $\Delta_{e/f} = qJ'(J'+1)$  yields the experimental estimate  $|q/d| = (0.9 \pm 0.2) \times 10^{-7} \text{ cm}^{-1}/\text{D}$  for the  $(4)^1\Pi(v'=2, J'=82)$  state.

The constructed “difference-based” potential energy curves  $U_i^{dif}(R)$  are presented in Fig. 3. For all treated excited states, the equilibrium molecular constants extracted from the  $U_i^{dif}$  potentials agree very well with their experimental (except the experimental  $T_e$  value for the  $(3)^1\Pi$  state [10]) and theoretical counterparts (see Table I). The resulting *ab initio* permanent dipole moments  $d^{ab}(R)$  for the four lowest  $^1\Pi$  states are presented in Fig. 4, while the relevant  $d_{v,J'}$  values are depicted on Fig. 5. The absolute value of the dipole moment estimate for RbCs  $(4)^1\Pi$  state converging to the Rb( $4d$ )+Cs( $6s$ ) limit is very close to those for the  $(2)^1\Pi$  state of NaK [19] and NaRb [20] dimers, while the sign of the dipole moment is opposite. It is worth mentioning that the minus sign corresponds to  $\text{Rb}^-\text{Cs}^+$  while the plus sign corresponds to the  $\text{Rb}^+\text{Cs}^-$  case.

The calculated *ab initio* angular coupling matrix elements  $L_{\Pi\sim\Sigma^+}^{ab}(R)$  between the  $(2,4)^1\Pi$  and low-lying  $^1\Sigma^+$  states of the  $^{85}\text{Rb}^{133}\text{Cs}$  isotopomer are presented in Fig. 6a,b while the corresponding  $q$ -factors are presented in Fig. 7. The abrupt changes of the  $L_{\Pi\sim\Sigma^+}^{ab}(R)$  functions belonging to the highest  $^1\Sigma^+$  states reproduce the avoided crossing effects of the corresponding adiabatic states. The Van-Vleck hypothesis of pure precession [22] fails completely for both  $(2,4)^1\Pi$  states since the strong dipolar RbCs core leads to the pronounced  $l$ -mixing effect even at small internuclear distances.

The calculated  $q = 5.9 \times 10^{-7} \text{ cm}^{-1}$  value for the  $(2)^1\Pi$  state corresponding to  $J' = 150$  (see Fig. 7) agrees remarkably well with its experimental counterpart  $q = 5.87 \times 10^{-7} \text{ cm}^{-1}$  extracted from the FTS spectra [7]. The calculated values  $q = 8.2 \times 10^{-7} \text{ cm}^{-1}$  and  $d = -6.9 \text{ D}$  for the  $(4)^1\Pi(v' = 2, J' = 82)$  state yield the ratio  $|q/d| = 1.2 \times 10^{-7} \text{ cm}^{-1}/\text{D}$ , which is not far from the obtained experimental value, though overshooting the latter slightly beyond the experimental 20% error. As far as calculations are concerned, the discrepancy could be most likely attributed to the theoretical  $q$ -factor overestimate caused by neglecting a significant contribution of the higher-lying bound and autoionising  $^1\Sigma^+$  states, as well as a spin-orbit perturbation arising from strong local interaction with the nearest triplet  $(6)^3\Sigma^+$  and  $(4)^3\Pi$  states.

#### V. ACKNOWLEDGMENTS

The authors are indebted to Prof. William C. Stwalley for suggesting these investigations, as well as for numerous helpful discussions. We are grateful to Dr. R. Kalendarev for assistance in the experiments. The work has been supported by the NATO SfP978029 *Optical Field Mapping* grant. The Moscow team is grateful for the support from the Russian Foundation for Basic Researches (grants N03-03-32805a and N03-03-32857a). The Riga team acknowledges the funding from the Latvian Science Council (grants No. 01.0264 and No. 04.1308), the support from Latvian Ministry of Education and Science (grants TOP 02-45 and ES 03-40), as well as appreciates the mobility opportunities provided by the EC 5<sup>th</sup> Frame Growth Grant G1MA-CT-2002-04063.

- 
- |  |  |
|--|--|
| <p>[1] H. Wang and W. C. Stwalley, J. Chem. Phys. <b>108</b>, 5767 (1998).</p> <p>[2] A. J. Kerman, J. M. Sage, S. Sainis, T. Bergeman, and D. De-Mille, Phys. Rev. Lett. 033004 (2004).</p> <p>[3] M. J. Jamieson, H. Sarbazi-Azad, H. Ouerdane, G.-H. Jeung, Y. S. Lee, and W. C. Lee, J. Phys. B: At., Mol. Opt. Phys. <b>36</b> (2003) 1085.</p> <p>[4] D. DeMille, Phys. Rev. Lett. <b>88</b>, 067901 (2002).</p> | <p>[5] H. Katô and H. Kobayashi, J. Chem. Phys. <b>79</b>, 123 (1983).</p> <p>[6] T. Gustavsson, C. Amiot, and J. Verges, Mol. Phys. <b>64</b>, 279 (1988).</p> <p>[7] T. Gustavsson, C. Amiot, and J. Verges, Chem. Phys. Lett. <b>143</b>, 101 (1988).</p> <p>[8] C. E. Fellows, R. F. Gutierrez, A. P. C. Campos, J. Verges and C. Amiot, J. Mol. Spectrosc. <b>197</b>, 19 (1999).</p> |
|--|--|

- [9] T. Gustavsson, C. Amiot, and J. Verges, *Mol. Phys.* **64**, 293 (1988).
- [10] B. Kim and K. Yoshihara, *J. Chem. Phys.* **100**, 1849 (1994).
- [11] Y. Yoon, Y. Lee, T. Kim, J. S. Ahn, Y. Jung, B. Kim, and S. Lee, *J. Chem. Phys.* **114**, 8926 (2001).
- [12] B. Kim and K. Yoshihara, *Chem. Phys. Lett.* **212**, 271 (1993).
- [13] T. Bergeman, C.E. Fellows, R.F. Gutterres, and C. Amiot, *Phys. Rev. A* **67**, 050501 (R)(2003).
- [14] D. Pavolini, T. Gustavsson, F. Spiegelmann, and J.P. Daudey, *J. Phys. B* **22**, 1721 (1989).
- [15] A. R. Allouche, M. Korek, K. Fakherddin, A. Chaalan, M. Dagher, F. Taher, M. Aubert-Frecon, *J. Phys. B* **33**, 2307 (2000).
- [16] H. Fahs, A. R. Allouche, M. Korek, and M. Aubert-Frecon, *J. Phys.* **B35**, 1501 (2002).
- [17] J. Derouard, H. Debontride, T. D. Nguyen, and N. Sadeghi, *J. Chem. Phys.* **90**, 5936 (1989).
- [18] M. Tamanis, M. Auzinsh, I. Klincare, O. Nikolayeva, A. V. Stolyarov, and R. Ferber, *J. Chem. Phys.* **106**, 2195 (1997).
- [19] M. Tamanis, M. Auzinsh, I. Klincare, O. Nikolayeva, R. Ferber, E. A. Pazyuk, A. V. Stolyarov, and A. Zaitsevskii, *Phys. Rev. A* **58**, 1932 (1998).
- [20] O. Nikolayeva, I. Klincare, M. Auzinsh, M. Tamanis, R. Ferber, E. A. Pazyuk, A. V. Stolyarov, A. Zaitsevskii, and R. Cimiraaglia, *J. Chem. Phys.* **113**, 4896 (2000).
- [21] M. Auzinsh, R. Ferber, O. Nikolayeva, N. Shafer-Ray, M. Tamanis, *J. Phys. D: Applied Physics* **34**, 624 (2001).
- [22] H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, New York, 1986).
- [23] M. Auzinsh and R. Ferber, *Optical Polarisation of Molecules*, (Cambridge University Press, Cambridge, 1996).
- [24] A. Zaitsevskii and J. P. Malrieu, *Theor. Chem. Acc.* **96**, 269-276 (1997).
- [25] A. Zaitsevskii and R. Cimiraaglia, *Int. J. Quantum Chem.* **73**, 395-401 (1999).
- [26] L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, *J. Chem. Phys.* **87**, 2812 (1987).
- [27] R. B. Ross, J. M. Powers, T. Atashroo, W. C. Ermler, *J. Chem. Phys.* **93**, 6654 (1990).
- [28] S. O. Adamson, A. Zaitsevskii, E. A. Pazyuk, A. V. Stolyarov, M. Tamanis, R. Ferber, R. Cimiraaglia, *J. Chem. Phys.* **113**, 8589-8593 (2000).
- [29] R. Shepard, I. Shavitt, R. M. Pitzer, D. C. Comeau, M. Pepper, H. Lischka, P. G. Szalay, R. Ahlrichs, F. B. Brown, and J. G. Zhao, *Int. J. Quantum Chem.*, **S22**, 149 (1988).
- [30] H. Lischka, R. Shepard, I. Shavitt, R. M. Pitzer, M. Dallos, Th. Müller, P. G. Szalay, F. B. Brown, R. Ahlrichs, H. J. Böhm, A. Chang, D. C. Comeau, R. Gdanitz, H. Dachsel, C. Ehrhardt, M. Ernzerhof, P. Höchtl, S. Irle, G. Kedziora, T. Kovar, V. Parasuk, M. J. M. Pepper, P. Scharf, H. Schiffer, M. Schindler, M. Schüler, M. Seth, E. A. Stahlberg, J.-G. Zhao, S. Yabushita, and Z. Zhang, COLUMBUS, an *ab initio* electronic structure program, release 5.8 (2001).
- [31] A. V. Stolyarov and V. I. Pupyshev, *Phys. Rev. A* **49**, 1693 (1994)

TABLE I: Comparison of the molecular constants derived by the present “difference-based” potentials for  $(2,4)^1\Pi$  and  $(2 \div 7)^1\Sigma^+$  states of  $^{85}\text{Rb}^{133}\text{Cs}$  with their experimental and theoretical counterparts.

State	Source	$T_e(\text{cm}^{-1})$	$R_e(\text{Å})$	$\omega_e(\text{cm}^{-1})$
	Present	13814	4.72	35.4
$(1)^1\Pi$	Calc.[15]	13753	4.68	38.6
	Present	14987	5.20	33.1
$(2)^1\Pi$	Exp.[9]	14963.6	5.164	32.93
	Calc.[15]	15046	5.12	33.4
	Present	17598	5.07	22.8
$(3)^1\Pi$	Exp.[10]	17418.9		22.53
	Calc.[15]	17633	5.06	20.4
	Present	20959	5.16	30.9
$(4)^1\Pi$	Exp.[9]	20897.0	5.117	30.24
	Calc.[15]	21034	5.07	30.7
	Present	10132	5.16	37.2
$(2)^1\Sigma^+$	Exp.[13]	10037.83	5.175	36.65
	Calc.[15]	10065	5.07	37.7
	Present	13061	5.54	29.3
$(3)^1\Sigma^+$	Exp.[9]	13052.7	5.526	28.48
	Calc.[15]	13060	5.43	28.8
	Present	16747	5.520	24.0
$(4)^1\Sigma^+$	Exp.[10]	16626.6		24.51
	Calc.[15]	16674	5.54	23.1
	Present	18551	4.95	40.1
$(5)^1\Sigma^+$	Exp.[11]	18564.6	4.951	39.19
	Calc.[15]	18562	4.87	41.4
	Present	19522	5.408	35.2
$(6)^1\Sigma^+$	Calc.[15]	19624	5.332	35.4
	Present	21252	5.17	35.3
$(7)^1\Sigma^+$	Exp.[9]	21230.9	5.118	35.04
	Calc.[15]	21273	5.07	35.3

- [32] E. A. Pazyuk, A. V. Stolyarov, and V. I. Pupyshev, *Chem. Phys. Lett.* **228**, 219 (1994)

### Captions to figures

Fig. 1. Fragment of the  $(4)^1\Pi \rightarrow X^1\Sigma^+$  RbCs LIF spectrum excited by 501.7 nm  $\text{Ar}^+$  laser line.

Fig. 2. Stark effect in the  $(4)^1\Pi(v' = 2, J' = 82)$  state of RbCs. Thin lines are obtained by Gaussian approximation; dashed lines are recovering the triplet structure. The insertion represents the excitation and observation geometry and polarization.

Fig. 3. Adiabatic “difference-based” potentials for the lowest excited  $(1\div 4)^1\Pi$  (solid lines) and  $(2\div 9)^1\Sigma^+$  (dashed lines) states of RbCs.

Fig. 4. *Ab initio* permanent electric dipole moments  $d^{ab}(R)$  for the  $(1\div 4)^1\Pi$  states of RbCs as dependent on

the internuclear distance  $R$ .

Fig. 5. Calculated permanent electric dipole moments  $d$  for the  $(1\div 4)^1\Pi$  states of RbCs as dependent on the vibrational  $v'$  and rotational  $J'$  quantum numbers.

Fig. 6. Non-adiabatic electronic matrix elements of the angular coupling  $L_{\Pi\Sigma}^{ab}(R)$  of the  $^{85}\text{Rb}^{133}\text{Cs}$  isotopomer; (a) – between the  $(2)^1\Pi$  and  $(1\div 7)^1\Sigma^+$  states; (b) – between the  $(4)^1\Pi$  and  $(1\div 9)^1\Sigma^+$  states.

Fig. 7. Calculated  $q$ -factors for the  $(2,4)^1\Pi$  states of RbCs as dependent on the vibrational  $v'$  and rotational  $J'$  quantum numbers.