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

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The article presents first experimental data on the Stark induced *e-f* mixing in the (4) $^1\Pi$ state of the $^{85}Rb^{133}Cs$ 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. The appearance of the "forbidden" lines in the laser-induced (4) $^1\Pi \rightarrow X\,^1\Pi^+$ fluorescence spectrum in the presence of an electric field allowed us to obtain, for the rovibronic $v'(J')=2(82)$ level of the (4) $^1\Pi$ state correlating to the Rb($4d$)+Cs($6s$) atomic limit, the ratio $q/d=0.9\times10^{-7}$ cm^{-1}/D with 20% experimental error. 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. The *ab initio* $d(R)$ estimates revealed large values of about $d\approx-7$ 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 with the present experimental value.

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I. INTRODUCTION

The RbCs molecule is considered among convenient species for formation of Bose-Einstein condensate (BEC) and ultracold heteronuclear molecules [1] since both cold Rb and Cs atoms can be feasibly prepared by diode lasers. Ultracold RbCs molecules have been recently produced in their electronically excited states [2] via photoassociation in a ca. 100 μK mixture of ^{85}Rb and ^{133}Cs atoms. In particular, the Stark effect was registered in the photoassociation experiments [2], allowing us to estimate the permanent dipole moment ($d=1.3$ D) of the 0^+ state dissociating to Rb($5S_{1/2}$) and 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 the Stark effect in polar alkali-metal dimers as the means to create 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 inverted perturbation approach (IPA) potential up to the dissociation limit were derived in Refs. [6–8] by Fourier-transform spectroscopy (FTS). Molecular constants and Rydberg-Klein-Rees (RKR) potentials for the electronically excited $(2,4,5)$ $^1\Pi$ and $(3,7)$ $^1\Pi^+$ 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 (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 semiempirical spin-orbit pseudopotential.

In the present paper, we report the *ab initio* calculations of permanent electric dipoles in the $(1-4)$ $^1\Pi$ 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 Λ-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 Λ 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 a Stark operator. It leads to the appearance of "forbidden" lines in the $^1\Pi \rightarrow {}^1\Sigma^+$ LIF spectrum, which in the presence of dc electric field contains the complete (P,Q,R)-triplet fluoresence 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 and 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 a ca. 1:1 mixture of natural Rb (containing 72% of ^{85}Rb and 28% of ^{87}Rb) and Cs

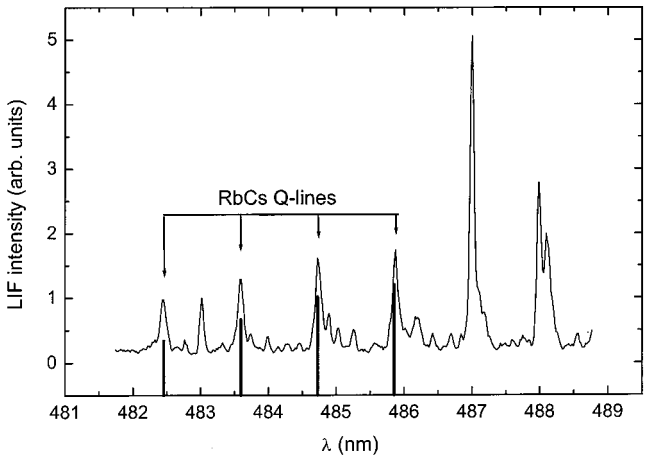

FIG. 1. Fragment of the (4) $^1\Pi \rightarrow X\,^1\Sigma^+$ RbCs LIF spectrum excited by a 501.7-nm Ar^+ laser line.

metals in a thermal alkali-resistant glass cell at the temperature ca. 570 K. An 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 slit widths, the 0.2 Å spectral resolution. Fluorescence was detected in the spectral range 480–490 nm by a FEU-79 photomultiplier operating in the photon-counting regime. An 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 ± 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 $^{85}Rb^{133}Cs$ 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 the inset in Fig. 2. The Stark mixing 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 a density matrix formalism for the interaction of cw broadband radiation with a diatomic molecule in the presence of an external electric field [18,23]. The experimental curve $I_f(E)/I_p(E)$ was fitted with respect to the single parameter $|\Delta_{e/f}/d|=0.61\times10^{-3}$ cm^{-1}/D. The value of inverse radiative lifetime of the excited level, $\Gamma=10^7$ sec^{-1}, was used in calculations. It was numerically proven that changes in $|\Delta_{e/f}/d|$ value do not exceed 1% when Γ varied within an order of magnitude. The uncertainties in the experimental I_f/I_p values, Stark plate gap, and electric field voltage lead to a 20% overall relative error estimate in the $\Delta_{e/f}/d$ ratio. The very low intensities of the forbidden lines have not allowed us to employ the direct $\Delta_{e/f}$ measurement by optical-radio-frequency double resonance [19,20].

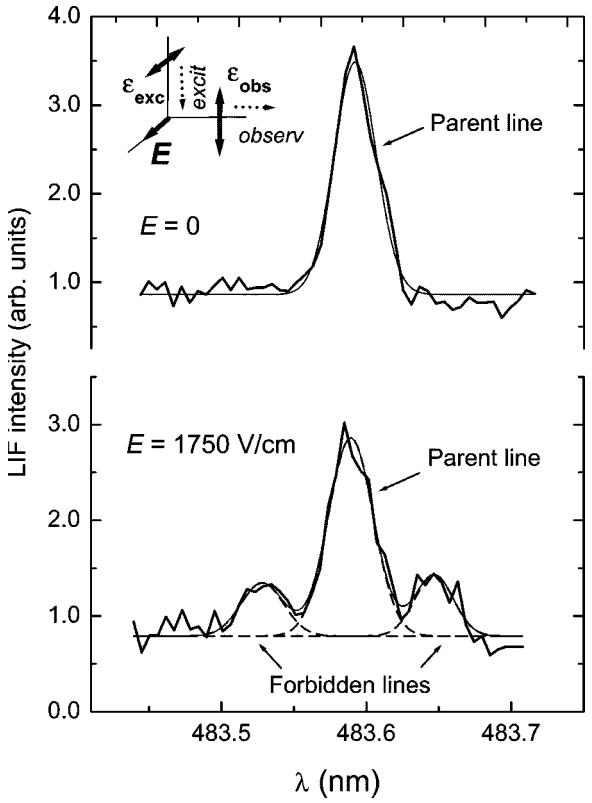

FIG. 2. Stark mixing in the (4) $^1\Pi(v'=2, J'=82)$ state of RbCs. Thin lines are obtained by Gaussian approximation; dashed lines are recovering the triplet structure. The insertion represents the excitation and observation geometry and polarization.

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 Λ-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 nine 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_rbcs.html for detailed information). Outer-core-like one-particle functions (molecular orbitals, MO's) were obtained via state-average multiconfigurational self-consistent-field (MCSCF) calculations on the lowest $^{1,3}\Sigma$ of RbCs and $^2\Sigma^+$ of $RbCs^+$ states; during the generation of the remainder MO's 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 diagonalized the state-selective effective Hamiltonian in the model space spanned by all possible distributions of two valence electrons among the valence and virtual MO's (full valence configuration interaction

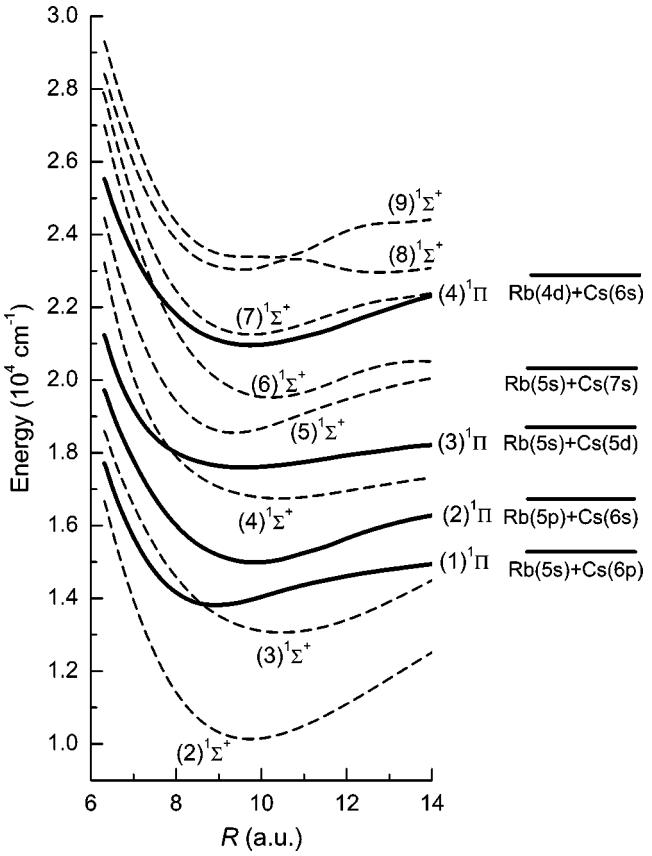

FIG. 3. Adiabatic "difference-based" potentials for the lowest excited $(1-4)\,^1\Pi$ (solid lines) and $(2-9)^1\Sigma^+$ (dashed lines) states of RbCs.

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 $L^{ab}_{\Pi\Sigma}(R)$ 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 MCSCF 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 (PDM's) on the vibrational v' and rotational J' quantum numbers was evaluated as the expectation value of the derived *ab initio* functions $d^{ab}(R)$: $d^{\Pi}_{vJ}=\langle v^{\Pi}_J|d^{ab}(R)|v^{\Pi}_J\rangle_R$, where $|v^{\Pi}_J\rangle$ are the adiabatic rovibrational wavefunctions for the $(1-4)\,^1\Pi$ states treated.

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

$$q^{\Pi}_{vJ}=\frac{1}{2\mu^2}\sum_{\Sigma^+}\sum_{v_\Sigma}\frac{|\langle v^{\Pi}_J|L^{ab}_{\Pi\Sigma}(R)/R^2|v^{\Sigma}_J\rangle_R|^2}{E^{\Pi}_{vJ}-E^{\Sigma}_{v'J}}, \qquad (1)$$

where μ is the reduced molecular mass while the E_{vJ} and $|v_J\rangle$ are the eigenvalues and eigenfunctions of the corresponding

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

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

adiabatic states. The summation was restricted by the lowest seven and nine $^1\Sigma^+$ states for the $2^1\Pi$ and $4^1\Pi$ states, 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 Eq. (1) over the vibrational states v_{Σ^+}. 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

$$q^{\Pi}_{vJ}\approx\frac{1}{2\mu^2}\left\langle v^{\Pi}_J\left|R^{-4}\sum_{\Sigma^+}\frac{|L^{ab}_{\Pi\Sigma}(R)|^2}{\Delta U^{ab}_{\Pi\Sigma}(R)}\right|v^{\Pi}_J\right\rangle_R, \qquad (2)$$

where $\Delta U^{ab}_{\Pi\Sigma}(R)=U^{ab}_{\Pi}(R)-U^{ab}_{\Sigma^+}(R)$ 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^{ab}_i, the adiabatic difference potentials for all treated excited states were constructed using the relation $U^{dif}_i(R)=U^{ab}_i(R)+\Delta U_X(R)$,

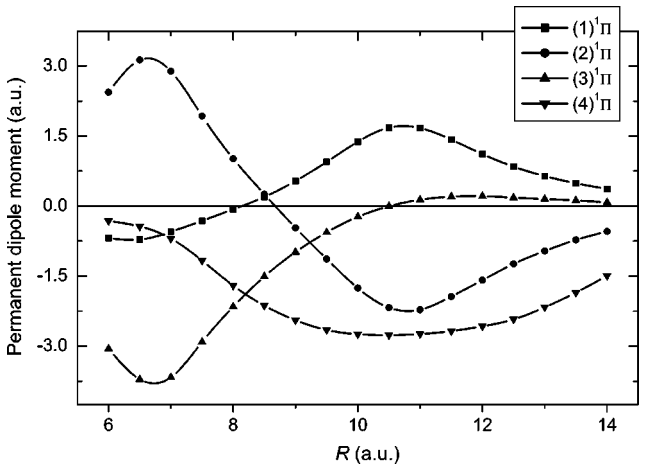

FIG. 4. *Ab initio* permanent electric dipole moments $d^{ab}(R)$ for the $(1-4)\ ^1\Pi$ states of RbCs as dependent on the internuclear distance R.

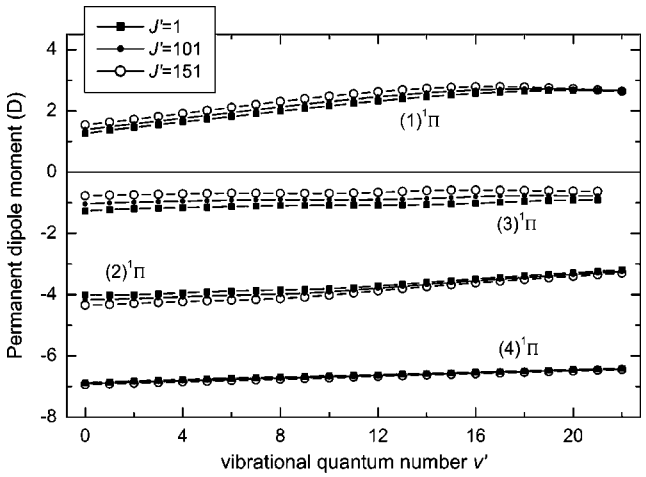

FIG. 5. Calculated permanent electric dipole moments d for the $(1-4)\ ^1\Pi$ states of RbCs as dependent on the vibrational v' and rotational J' quantum numbers.

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 wave functions $|v_J\rangle$ 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 $(2,4)\ ^1\Sigma^+$ [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

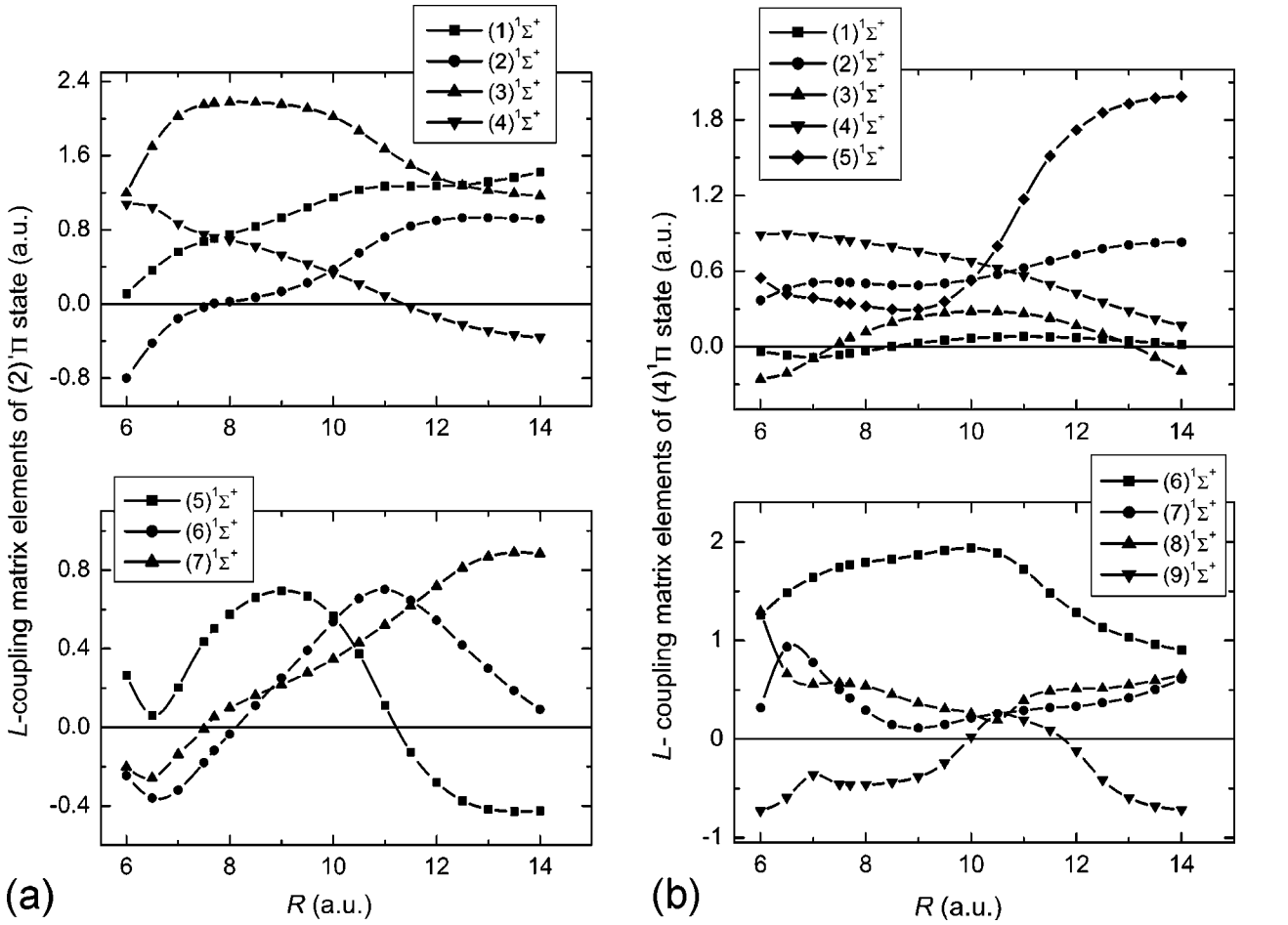

FIG. 6. Nonadiabatic electronic matrix elements of the angular coupling $L_{\Pi\Sigma}^{ab}(R)$ of the $^{85}Rb^{133}Cs$ isotopomer (a) between the (2) $^1\Pi$ and $(1-7)\ ^1\Sigma^+$ states and (b) between the (4) $^1\Pi$ and $(1-9)\ ^1\Sigma^+$ states.

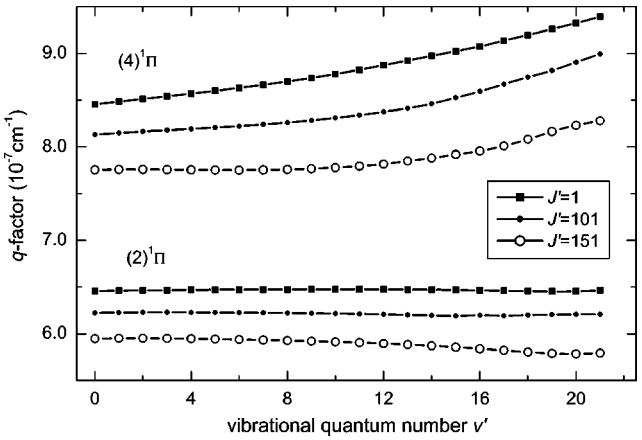

FIG. 7. Calculated q factors for the $(2,4)\ ^1\Pi$ states of RbCs as dependent on the vibrational v' and rotational J' quantum numbers.

remainder $(1,3)\ ^1\Sigma^+$ and $(4,6,8,9)\ ^1\Sigma^+$ states.

IV. RESULTS AND DISCUSSION

The representation of the Λ splitting as $\Delta_{e/f}=qJ'(J'+1)$ yields the experimental estimate $|q/d|=(0.9\pm0.2)\times10^{-7}$ cm^{-1}/D for the (4) $^1\Pi(v'=2,J'=82)$ state.

The constructed "difference-based" potential energy curves $U^{dif}(R)$ 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 in Fig. 5. The absolute value of the dipole moment estimate for a RbCs (4) $^1\Pi$ state converging to the Rb$(4d)$+Cs$(6s)$ limit is very close to those for the $(2)D\ ^1\Pi$ 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 Rb^-Cs^+ while the plus sign corresponds to the Rb^+Cs^- case.

The calculated *ab initio* angular coupling matrix elements $L^{ab}_{\Pi\sim\Sigma^+}(R)$ between the $(2,4)\ ^1\Pi$ and low-lying $^1\Sigma^+$ states of the $^{85}Rb^{133}Cs$ isotopomer are presented in Figs. 6(a) and 6(b). The abrupt changes of the $L^{ab}_{\Pi\sim\Sigma^+}(R)$ functions belonging to the highest $^1\Sigma^+$ states reproduce the avoided crossing effects of the corresponding adiabatic states. The corresponding q factors are presented in Fig. 7. The calculated $q=5.9\times10^{-7}$ cm^{-1} value for the (2) $^1\Pi$ state corresponding to $J'=150$ (see Fig. 7) agrees remarkably well with its experimental counterpart $q=5.87\times10^{-7}$ cm^{-1} extracted from the FTS spectra [7]. The calculated values $q=8.2\times10^{-7}$ cm^{-1} and $d=-6.9$ D for the (4) $^1\Pi(v'=2,J'=82)$ state yield the ratio $|q/d|=1.2\times10^{-7}$ cm^{-1}/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 a strong local interaction with the nearest triplet (6) $^3\Sigma^+$ and (4) $^3\Pi$ states.

It should be noted that the widespread Van Vleck hypothesis of a "pure precession" and "unique perturber" approximation [22] yields the q values 4.5×10^{-7} and 2.9×10^{-6} cm^{-1} for (2) $^1\Pi$ and (4) $^1\Pi$ states, respectively, which differ considerably from the *ab initio* calculations presented in Fig. 7. The observed breakdown of the "pure precession" hypothesis for these states seems to be attributed to the pronounced l-mixing effect which should take place in the excited states converging to strong dipolar cores [33]. Futhermore, the violation of the Van Vleck hypothesis increases for the NaK, NaRb, and RbCs dimers since a shift of the center mass origin with respect to nonzero angular momentum atom increases in this progression of molecules. Moreover, both the Van Vleck hypothesis breakdown and high density of the excited states in heavy alkali-metal dimers apparently lead to a fail of the "unique perturber" approximation as well. In particular, the (7) $^1\Sigma^+$ state converging to the $6s$(Rb) $+6s$(Cs) limit (see Fig. 1) gives the pronounced partial contribution to the q factor of the nearest (4) $^1\Pi$ state in spite of rather small L-coupling matrix element [see Fig. 4(b)].

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[1] H. Wang and W. C. Stwalley, J. Chem. Phys. **108**, 5767 (1998).
[2] A. J. Kerman, J. M. Sage, S. Sainis, T. Bergeman, and D. DeMille, Phys. Rev. Lett. **92**, 033004 (2004).
[3] M. J. Jamieson, H. Sarbazi-Azad, H. Ouerdane, G.-H. Jeung, Y. S. Lee, and W. C. Lee, J. Phys. B **36**, 1085 (2003).
[4] D. DeMille, Phys. Rev. Lett. **88**, 067901 (2002).
[5] H. Katô and H. Kobayashi, J. Chem. Phys. **79**, 123 (1983).

[6] T. Gustavsson, C. Amiot, and J. Verges, Mol. Phys. **64**, 279 (1988).
[7] T. Gustavsson, C. Amiot, and J. Verges, Chem. Phys. Lett. **143**, 101 (1988).
[8] C. E. Fellows, R. F. Gutteres, A. P. C. Campos, J. Verges, and C. Amiot, J. Mol. Spectrosc. **197**, 19 (1999).
[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, and M. Aubert-Frecon, J. Phys. B **33**, 2307 (2000).
[16] H. Fahs, A. R. Allouche, M. Korek, and M. Aubert-Frecon, J. Phys. B **35**, 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. Cimiraglia, J. Chem. Phys. **113**, 4896 (2000).
[21] M. Auzinsh, R. Ferber, O. Nikolayeva, N. Shafer-Ray, and M. Tamanis, J. Phys. D **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, England, 1996).
[24] A. Zaitsevskii and J. P. Malrieu, Theor. Chim. Acta **96**, 269 (1997).
[25] A. Zaitsevskii and R. Cimiraglia, Int. J. Quantum Chem. **73**, 395 (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, and 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, and R. Cimiraglia, J. Chem. Phys. **113**, 8589 (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., Quantum Chem. Symp. **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).
[32] E. A. Pazyuk, A. V. Stolyarov, and V. I. Pupyshev, Chem. Phys. Lett. **228**, 219 (1994).
[33] M. S. Child, in *Molecular Rydberg Dynamics*, The Royal Society Discussion (Imperial College Press, London, 1999), pp. 1–16.