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Ab initio multi-reference perturbation theory calculations of the ground and some excited electronic states of the RbYb molecule

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ABSTRACT

The potential energy curves of the ground and twelve low-lying excited electronic states of the RbYb molecule have been calculated using the multi-reference perturbation theory method at the CASSCF/XMCQDPT2 level of theory including the spin-orbit coupling. The electronic term energies, equilibrium internuclear distances, dissociation energies, transition dipole moments, the sequences of vibrational energies, the harmonic vibrational frequencies, and the Franck–Condon factors have been predicted. The potential energy curves at the asymptotic limits are in a good agreement with the experimental data for rubidium and ytterbium atoms. The obtained data would be useful for spectral experiments with RbYb molecules.

1. Introduction

The RbYb molecule belongs to heteronuclear diatomics, which due to the availability of an unpaired electron have both electric and magnetic permanent dipole moments. This makes possible trapping and manipulating of the weakly bound RbYb molecules in the ground $X^2\Sigma^+_{1/2}$ state using electric as well as magnetic fields [1] enabling their usage in many applications under cold and ultracold conditions [2].

The electronic states of the RbYb molecule were studied experimentally in [1,3] and theoretically in [4–8]. Some experimental difficulties preventing the formation of RbYb molecules are discussed by Tassy et al. [9] and Baumer et al. [10]. Nemitz et al. [1] obtained the energies of 15 vibrational states near the dissociation limit of the excited $1^2\Pi_{1/2}$ state of the ^{87}Rb^{176}Yb and ^{87}Rb^{174}Yb molecules. The energies of 7 vibrational states near the dissociation limit of the ground $X^2\Sigma^+_{1/2}$ state of the ^{87}Rb^{176}Yb molecule are determined by Münchow et al. [3].

Ab initio calculations of the RbYb electronic states are performed in the multi-reference CASSCF/MRCI (Complete Active Space Self-Consistent Field/Multi-Reference Configuration Interaction) [4,6] and CASSCF/MRCC (Multi-Reference Coupled Cluster) [4,5,7,8] approximations. It is worth mentioning that theoretical data in Refs. [4–8] for the dissociation energy D_e of the ground $X^2\Sigma^+_{1/2}$ state differ substantially. Sørensen et al. [4] obtained (in different basis sets and approximations) D_e in the range 591–868 cm^{-1}, whereas Meyer and Bohn [5] indicated only 193 cm^{-1}. The value of the D_e according to Tohme and Korek [6] is close to 700 cm^{-1}. Borkowski et al. [7] in two different calculations have given 704 and 786 cm^{-1}. Brue and Hutson [8] obtained D_e = 656 cm^{-1}. The calculated equilibrium internuclear distance R_e of the ground $X^2\Sigma^+_{1/2}$ state is also differing: 4.89–4.67 [4], 5.41 [5], 4.99889 [6], 4.77 and 4.68 [7], 4.91 Å [8].

Recently [11,12] we have shown that the *ab initio* calculations at the CASSCF/XMCQDPT2 (Extended Multi-Configuration Quasi-Degenerate 2nd Order Perturbation Theory) [13] level of theory predict the spectroscopic parameters of the ground state for the KRb molecule with a high accuracy. For the dissociation energy D_e of the ground $X^1\Sigma^+$ state, we have 4213.1 cm^{-1} that is in a better agreement with the experimental value (4217.815 cm^{-1} [14]) than those in other *ab initio* calculations (for details see [12]). The calculated equilibrium internuclear distance of the KRb ground $X^1\Sigma^+$ state (R_e = 4.07581 Å) also agrees considerably well with the experimental data by Pashov et al. [14] (R_e = 4.06770 Å). We assume that the CASSCF/XMCQDPT2 level of theory is well applicable to the electronic structure calculations of heavy diatomic molecules. Especially high accuracy is expected for the ground electronic state.

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The main goals of this work are: (i) to calculate the potential energy curves (PECs) of the ground and some low-lying excited states of the RbYb molecule at the multi-reference perturbation level of theory including the spin-orbit coupling (SOC) and (ii) to determine other spectroscopic characteristics of the electronic states (transition dipoles, vibrational energies, Franck–Condon factors, etc.). The main attention is paid to the ground $X^2\Sigma^+_{1/2}$ and low-lying excited $1^2\Pi_{1/2}$, $1^2\Pi_{3/2}$, and $2^2\Sigma^+_{1/2}$ states of the RbYb molecule.

2. Computations

The electronic configuration and the ground state term for the rubidium atom are [Kr]5 s and $^2S_{1/2}$, respectively. The first three excited configurations, atomic states, and their energies of the Rb atom are: 5p → $^2P_{1/2}$ (12,578.950 cm^{-1}), $^2P_{3/2}$ (12,816.545 cm^{-1}); 4d → $^2D_{5/2}$ (19 355.203 cm^{-1}), $^2D_{3/2}$ (19,355.649 cm^{-1}), and 6 s → $^2S_{1/2}$ (20,132.510 cm^{-1}) [15]. The SOC splittings of the ^2P and ^2D terms are 237.595 and 0.446 cm^{-1}, respectively.

The electronic configuration and the ground state term for the ytterbium atom are [Xe]4f^{14}6s^2 and $^1S_0$, respectively. The first excited configuration, appropriate triplet and singlet terms, and energies of the states for the Yb atom are: 4f^{14}6s6p → $^3P_0$ (17,288.499 cm^{-1}), $^3P_1$ (17,992.007 cm^{-1}), $^3P_2$ (19,710.388 cm^{-1}), and ^1P (25 068.222 cm^{-1}) [15]. The SOC splittings of the triplet ^3P term (703.508 and 1718.381 cm^{-1}) demonstrate violation of the Landé interval rule.

The next excited term (7/2, 3/2)$_{2,3,4,5}$ corresponds to the 4f^{13}5d^{1}6s^2 excited configuration with energies of the states lying within the range 23,288–28,184 cm^{-1} [15]. The triplet $^3D_{1,2,3}$ term originating from the 4f^{14}5d6 s configuration with the energies ranging 24,489–25,271 cm^{-1} [15] and the ^1P term (see above) are located between the components of the (7/2, 3/2)$_{2,3,4,5}$ term. Consequently, calculations of the molecular electronic states which correlate to the dissociation limits with given or higher excited configurations of the Yb atom require consideration of the f-electrons in the active space. Such states are not considered here.

The PECs calculations have been performed for the doublet and quartet states corresponding to the three lowest dissociation limits: Rb(5 s) + Yb(6s^2) (limit I), Rb(5p) + Yb(6s^2) (limit II), and Rb (5s) + Yb(6s6p, only triplet term) (limit III). Note that the ^2D term of the Rb atom lies between the $^3P_1$ and $^3P_2$ components of the ^3P term of the Yb atom. Consequently, it is assumed that the molecular electronic terms corresponding to the Rb(4d) + Yb(6s^2) and Rb(6s) + Yb(6s^2) dissociation limits are strongly perturbed by the terms corresponding to the Rb(5s) + Yb(6s6p) dissociation limit. Since the terms corresponding to the Rb(5s) + Yb (4f^{13}5d^{1}6s^2) dissociation limit, which must be directly above the above-mentioned terms, are not included into the calculations, the terms corresponding to the Rb(4d) + Yb(6s^2) and Rb(6s) + Yb (6s^2) dissociation limits are pushed up. Consequently, if excitations of the f-electrons of the Yb atom are not taken into account in the active space, PECs of these terms [6] will be of the artifact character.

Table 1
Molecular spectroscopic constants of ^{85}Rb^{174}Yb molecule.

Term		T_e, cm^{-1}	R_e, Å	ω_e, cm^{-1}	D_e, cm^{-1}	Asymptotic limit, cm^{-1}	
$^{(2S+1)}\Lambda_\Omega$	$(n)\Omega$					Experimental[a]	Calculated
$X^2\Sigma^+_{1/2}$	(1)1/2	−531.1 −865[b] −844[c] −193[d] ∼−700[e] −785.8[f] −704.5[g] −656.2[h]	4.857 4.68 4.70[c] 5.41[d] 4.99889[e] 4.68[f] 4.77[g] 4.91[h]	36.397 29.751[b] 29.458[c] 12.6[d] 27.819[e] 28.81[f] 26.58[g]	531.1 865[b] 844[c] 193[d] ∼700[e] 785.8[f] 704.5[g] 656.2[h]	0.0	0.0
$1^2\Pi_{1/2}$	(2)1/2	5986.2 4929[b] 4975[c]	3.881 3.91[b] 3.91[c] 3.91[d]	73.939 69.294[b] 69.441[c] 70.9[d]	6592.8 7735[b] 7688[c] 3590[d]	12578.950	12579.0 12664[b] 12663[c]
$1^2\Pi_{3/2}$	(1)3/2	7028.1 5716[b] 5748[c]	3.910 3.93[b] 3.94[c] 3.98[d]	72.378 69.322[b] 69.181[c] 65.4[d]	5788.3 7164[b] 7131[c] 3120[d]	12816.545	12816.4 12880[b] 12879[c]
$2^2\Sigma^+_{1/2}$	(3)1/2	9843.3 8461[b] 8385[c]	4.413 4.46[b] 4.46[c] 4.54[d]	50.218 52.789[b] 52.284[c] 33.9[d]	2971.7 4423[b] 4388[c] 1026[d]		12815.0 12884[b] 12883[c]
$2^2\Pi_{1/2}$	(4)1/2	13395.3	4.396	42.088	3266.4	17288.499	16661.7
$1^4\Pi_{1/2}$	(5)1/2	14732.1	4.838	61.068	2735.7	17992.007	17467.8
$2^2\Pi_{3/2}$	(2)3/2	13915.7	4.430	42.582	3553.2		17468.9
$1^4\Pi_{-1/2}$	(1)−1/2	15746.0	4.460	57.889	1723.5		17469.5
$3^2\Sigma^+_{1/2}$	(6)1/2	15230.1	4.385	48.023	3851.2	19710.388	19081.3
$1^4\Pi_{3/2}$	(3)3/2	16445.7	4.438	43.712	2636.3		19082.0
$1^4\Sigma^+_{1/2}$	(7)1/2	18467.8	5.594	23.156	615.0		19082.8
$1^4\Pi_{5/2}$	(1)5/2	16929.0	4.429	44.807	2154.1		19083.1
$1^4\Sigma^+_{3/2}$	(4)3/2	18380.7	5.574	26.144	703.8		19084.5

[a] NIST [15].
[b] Sørensen et al. [4] without counterpoise correction.
[c] Sørensen et al. [4] with counterpoise correction.
[d] Meyer and Bohn [5].
[e] Tohme and Korek [6].
[f] Borkowski et al. [7] with all-electron basis set.
[g] Borkowski et al. [7] with ECP basis set.
[h] Brue and Hutson [8].

The ground $X^2\Sigma^+$ state corresponds to the asymptotic limit I; the doublet $2^2\Sigma^+$ and $1^2\Pi$ states correspond to the asymptotic limit II; the doublet $3^2\Sigma^+$, $2^2\Pi$ states, and the quartet $1^4\Sigma^+$ and $1^4\Pi$ states correspond to the asymptotic limit III. When SOC is taken into account, the $X^2\Sigma^+$, $2^2\Sigma^+$ and $3^2\Sigma^+$ states correspond to the $X^2\Sigma^+_{1/2}$, $2^2\Sigma^+_{1/2}$ and $3^2\Sigma^+_{1/2}$ states, respectively; the $1^2\Pi$ and $2^2\Pi$ states split into the $1^2\Pi_{3/2}$, $1^2\Pi_{1/2}$ and $2^2\Pi_{3/2}$, $2^2\Pi_{1/2}$ states, respectively; the $1^4\Sigma^+$ state splits into the $1^4\Sigma^+_{3/2}$ and $1^4\Sigma^+_{1/2}$ states; the $1^4\Pi$ state splits into the $1^4\Pi_{5/2}$, $1^4\Pi_{3/2}$, $1^4\Pi_{1/2}$ and $1^4\Pi_{-1/2}$ states. Note that, since the spin-orbit coupling mixes states of different multiplicity, the $^{(2S+1)}\Lambda_\Omega$ designation is rather conditional in character, especially for the states belonging to the asymptotic limit III. Then $(n)\Omega$ designation, where n is a number of the state with the given Ω, is more appropriate. The $^{(2S+1)}\Lambda_\Omega$ designation is used here to emphasize the relationship between the spin-mixed states and the spin-free ones, and hence such designation sometimes is useful. Both designations ($^{(2S+1)}\Lambda_\Omega$ and $(n)\Omega$) are given in Table 1.

The small core Stuttgart RSC ECP [16] and the large core Stuttgart RLC ECP [17] for rubidium and ytterbium atoms, respectively, have been used in our calculations. The Gaussian basis sets used are: (13s10p5d3f1g) → [8s7p5d3f1g] (ECP28MDF) for rubidium atom [16] and (7s7p6d) (ECP60MDF) for ytterbium atom [17].

First, the CASSCF calculations with the state-averaged (SA) procedure were done. The active space for the CASSCF calculations was 3 electrons in 18 orbitals. The SA procedure was realized for 5 doublet and 2 quartet states. The SA-CASSCF(3,18) calculations were performed pointwisely by steps of 0.05, 0.10, 0.25, and 0.50 Å for the internuclear distances ranging 3.00–6.00, 6.00–8.00, 8.00–9.00, and 9.00–20.00 Å, respectively.

Then the calculations for doublet and quartet states were performed in the XMCQDPT2 [13] approximation. All the eight lowest double occupied orbitals were included in the perturbation based calculations. The ISA shift of 0.048 [18] was used for the present approach. The dimensions of the effective Hamiltonian are: 9 × 9 and 5 × 5 for doublet and quartet states, respectively.

Finally, the spin-orbit coupling (SOC) calculations were performed with the one-electron Pauli–Breit operator. The effective nuclear charges (see, for example, [19–21]) are: 2035.0 and 8925.0 for the rubidium and ytterbium atoms, respectively. Large values of Z_{eff} should compensate errors of the expectation value $\langle 1/r^3 \rangle$ in the small r region arising with the use of the ECP basis sets [21].

So, the following parameters of the *ab initio* calculations at the MRPT + SOC level of theory influence the calculation accuracy: a number of the states considered in the perturbation theory method [12] (i); qualitative composition (Σ, Π, Δ) of the above-mentioned states [12] (ii); the energy denominator shift (EDS) for the intruder state avoidance (ISA) [12,18] (iii), and Z_{eff} values [21] (iv). These parameters allow one to vary the energies of the low-lying atomic states, and the optimal choice of these parameters provides the required accuracy for the characteristics of the low-lying electronic molecular states.

All these calculations were performed using the Firefly quantum chemical package [22]. The electronic energy terms T_e and the equilibrium internuclear distances R_e are obtained using the fourth degree polynomial approximation of the *ab initio* PECs near their minima.

The transition dipole moments (TDMs) are computed based on the CASSCF functions at the CASSCF/XMCQDPT2 + SOC level of theory. The calculations of the TDMs are performed using the GAMESS quantum chemical package [23].

The calculations of the vibrational states energies and the Franck–Condon factors are performed using the LEVEL program package [24].

3. Results and discussion

3.1. Electronic states

The calculated PECs versus internuclear distances are shown in Fig. 1 and are also given in the supplementary material. The calcu-

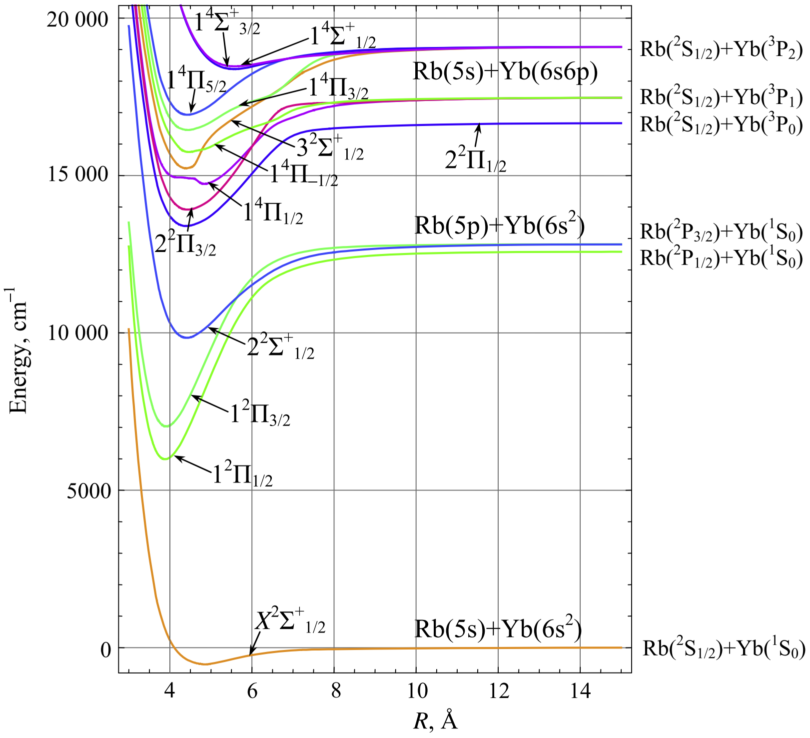


Fig. 1. The low-lying terms of the RbYb molecule calculated at the CASSCF(3,18)/XMCQDPT2 + SOC level of theory.

lated molecular spectroscopic constants (the electronic term energy T_e, the equilibrium internuclear distance R_e, the dissociation energy D_e, and the harmonic vibrational frequency ω_e) are presented and compared with the previous theoretical results in Table 1.

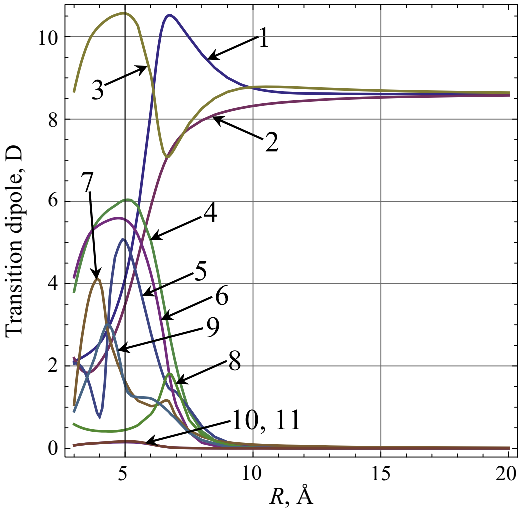


Fig. 2. Calculated transition dipole moments for the transitions from the ground (1) 1/2 state to the states (2)1/2 (1), (1)3/2 (2), (3)1/2 (3), (4)1/2 (4), (5)1/2 (5), (2)3/2 (6), (1)–1/2 (7), (3)3/2 (8), (6)1/2 (9), (7)1/2 (10), and (4)3/2 (11).

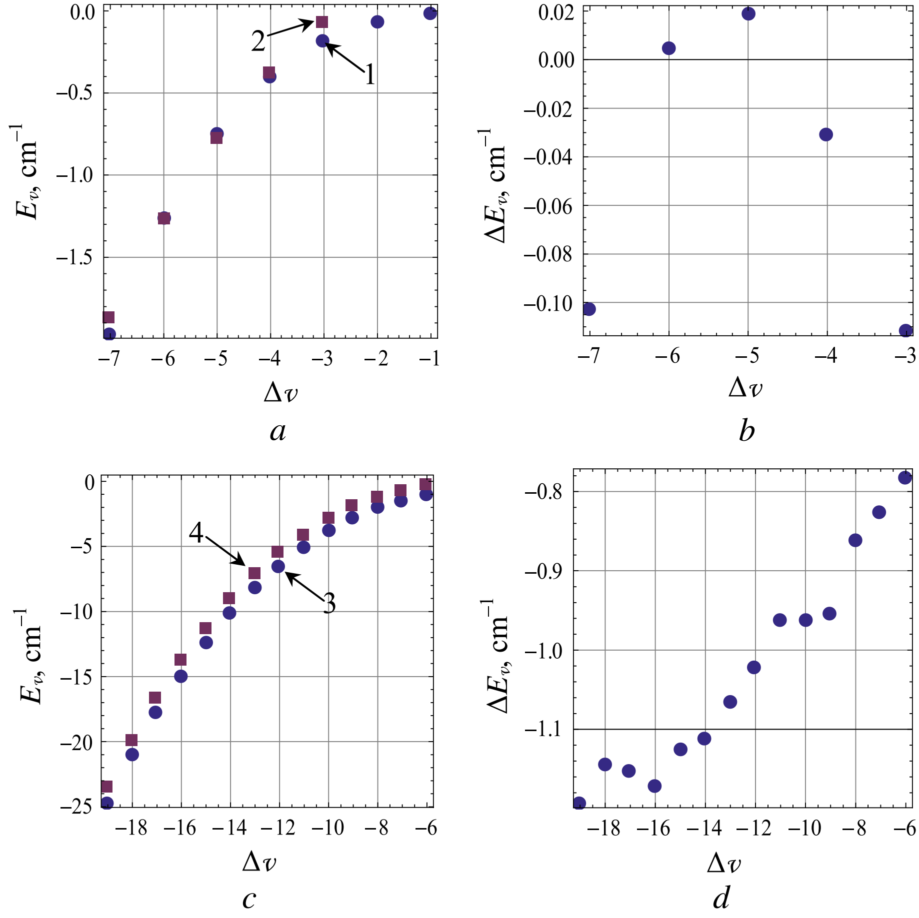
For the PECs of the asymptotic limit II at the internuclear distance of 20 Å, we have 12579.0, 12815.0, and 12816.4 cm^{-1} ($1^2\Pi_{1/2}$, $2^2\Sigma^+_{1/2}$, and $1^2\Pi_{3/2}$ states, respectively) with the SOC splitting that equals 237.4 cm^{-1}. As can be seen from Table 1, these values are in a good agreement with the NIST [15] experimental data (12578.950, 12816.545 and 237.595 cm^{-1}). This fact can be a criterion pointing to the adequacy of the determined spectroscopic parameters for the ground $X^2\Sigma^+_{1/2}$ and excited $1^2\Pi_{1/2}$, $2^2\Sigma^+_{1/2}$, and $1^2\Pi_{3/2}$ states.

Our calculated molecular constants D_e and R_e for the ground electronic state $X^2\Sigma^+_{1/2}$ (D_e = 531.1 cm^{-1}, R_e = 4.857 Å) are approximately intermediate between the results of Sørensen et al. [4] (865 cm^{-1}, 4.68 Å) and Meyer and Bohn [5] (193 cm^{-1}, 5.41 Å), being the closest to the data of Brue and Hutson [8] (656.2 cm^{-1}, 4.91 Å).

Our calculated T_e values of the $1^2\Pi_{1/2}$, $2^2\Sigma^+_{1/2}$ and $1^2\Pi_{3/2}$ states are higher than those of Sørensen et al. [4]. And, since the asymptotic behavior of these PECs in our and Sørensen's [4] calculations differs slightly, our calculated D_e values are lower than those of Sørensen et al. [4] (see Table 1). The equilibrium internuclear distances of the PECs of $1^2\Pi_{1/2}$, $2^2\Sigma^+_{1/2}$ and $1^2\Pi_{3/2}$ states obtained in our calculations are similar to the values of Sørensen et al. [4].

PECs of the asymptotic limit III are underestimated approximately by 626 cm^{-1} relative to the experimental energies [15] and the calculated total SOC splitting (2422.8 cm^{-1}) of this limit corresponds to the experimental [15] value (2421.889 cm^{-1}).

The calculated TDMs for the transitions from the ground state to the all spin-mixed excited states with the $\Delta\Omega$ = 0, ±1 selection rules as the functions of internuclear distances are shown in Fig. 2. Near the dissociation limits only TDMs in the case of the



a *b*

c *d*

Fig. 3. The vibrational energy E_v (*a*, *c*) and vibrational energy differences $\Delta E_v = E_v(\text{exper}) - E_v(\text{calc})$ (*b*, *d*) for the ground $X^2\Sigma^+_{1/2}$ (*a*, *b*) and first excited $1^2\Pi_{1/2}$ (*c*, *d*) states of the ^{87}Rb^{176}Yb molecule: (1) Münchow et al. [3], (3) Nemitz et al. [1], (2), and (4) the present calculations (see details in the text).

limit II are nonzero in conformity with the selection rules for the atomic transitions.

3.2. Vibrational states

The ^{85}Rb^{174}Yb molecule is the most abundant isopotomer (23%) among 14 natural isotopomers of the title molecule. Thus, the vibrational energies for the ^{85}Rb^{174}Yb molecule (and some other isotopomers) are calculated for all spin-mixed PECs up to the dissociation limit of the respective state, and the harmonic vibrational frequencies are also obtained (see Table 1). For the ground $X^2\Sigma^+_{1/2}$ and excited $1^2\Pi_{1/2}$, $1^2\Pi_{3/2}$, and $2^2\Sigma^+_{1/2}$ states we have 46, 168, 143 and 126 vibrational levels, respectively. For all of these states, the obtained ω_e values are the largest among all the earlier calculated values (see Table 1).

Since the experimental data for the vibrational states of the RbYb molecule are few in number, we compare the calculated energies of the weakly-bound vibrational states for the ground and for the first excited electronic states near the dissociation limits with the experimental data of Münchow et al. [3] and Nemitz et al. [1] in the case of ^{87}Rb^{176}Yb isotopomer. The results are presented in Fig. 3. Here $\Delta v = v - v_{max}$ is the relative vibrational quantum number and v_{max} is the vibrational quantum number of the last bound state.

The ground state PEC has a shallow well and hence PEC has a sloping behavior near the dissociation limit. Since our calculations are limited to 20 Å, a faster convergence of the vibrational states to the dissociation limit than that observed in the experiment is predicted [3]. So, the calculated energy of the v_{max} vibrational state is artificially overestimated relative to the lower vibrational states. In Fig. 3a and b we compare the calculated energies with Δv and the corresponding experimental values with $\Delta v - 2$. For the first excited $1^2\Pi_{1/2}$ state, a more exact agreement between the calculated and experimental [1] vibrational energies for the same Δv values is observed (Fig. 3c and d).

3.3. Franck–Condon factors

Basing on our *ab initio* PECs and calculated vibrational eigenfunctions, we predict the Franck–Condon factors (FCFs) between the relevant states of the ^{85}Rb^{174}Yb molecule. FCFs have been calculated for the rovibronic transitions between the all spin-mixed electronic states with the $\Delta\Omega = 0, \pm1$ selection rules. These calculations are performed for the transitions between the fixed vibrational level v′ of the upper electronic state and a sequence of vibrational levels v“ of the lower electronic state (applying the selection rules $\Delta J = 0$ or $\Delta J = \pm1$).

The selected FCFs between the vibrational levels of the first three exited states and the vibrational levels of the ground state with $\Delta J = 0$ selection rule are presented in Fig. 4. FCFs shown here are calculated for the transitions from the lowest vibrational levels (v′ = 0. . .4) of the excited electronic states (Fig. 4a, d, g) (1), for the

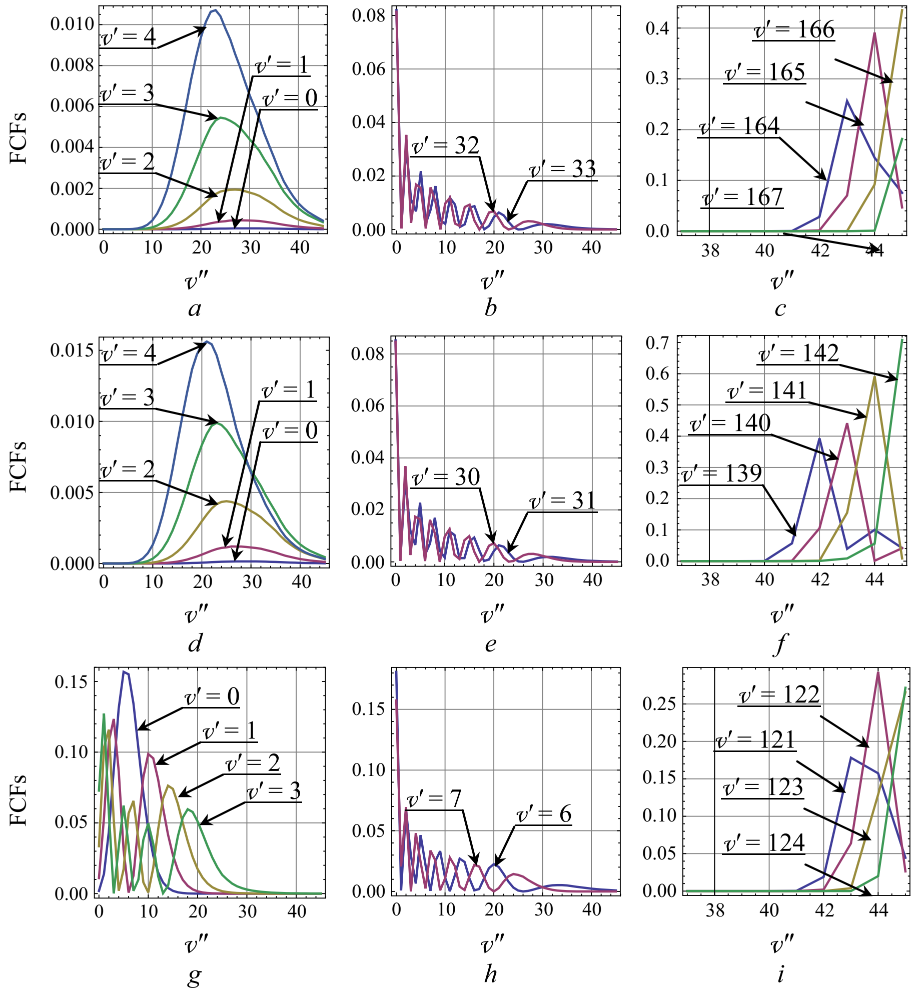


Fig. 4. The Franck–Condon factors for the $X^2\Sigma^+_{1/2} \leftarrow 1^2\Pi_{1/2}$ transitions (*a–c*), for the $X^2\Sigma^+_{1/2} \leftarrow 1^2\Pi_{3/2}$ transitions (*d–f*), and for the $X^2\Sigma^+_{1/2} \leftarrow 2^2\Sigma^+_{1/2}$ transitions (*g–i*) calculated with the $\Delta J = 0$ selection rule for the ^{87}Rb^{176}Yb molecule.

transitions with the largest FCFs to the ground rovibronic $X^2\Sigma^+_{1/2}$ (v" = 0, *J* = 0) state (Fig. 4b, e, *h*) (2), and for the transitions with the largest values of all possible FCFs (Fig. 4c, f, *i*) (3).

The FCFs distributions for the $X^2\Sigma^+_{1/2} \leftarrow 1^2\Pi_{1/2}$ and $X^2\Sigma^+_{1/2} \leftarrow 1^2\Pi_{3/2}$ transitions have a similar character (see Fig. 4a–f). The largest values of FCFs for the transitions to the "absolute" ground state $X^2\Sigma^+_{1/2}$ (v" = 0, *J* = 0) are about 0.08 with v′ = 28…34. Note that the rovibronic transitions from the weakly-bound vibrational states near the dissociation limits of the excited electronic states (v′ = 160…166 for $1^2\Pi_{1/2}$ state and v′ = 135…142 for $1^2\Pi_{3/2}$ state) to similar vibrational states of the ground electronic state (v" = 40…46) are most probable.

For the $X^2\Sigma^+_{1/2} \leftarrow 2^2\Sigma^+_{1/2}$ transitions to the "absolute" ground state $X^2\Sigma^+_{1/2}$ (v" = 0, *J* = 0), the largest FCFs correspond to the transitions from the $2^2\Sigma^+_{1/2}$ (v′ = 4…10) vibronic states with FCFs on the order of 0.1. Taking into account that the predicted average value of TDM for the $2^2\Sigma^+ \leftarrow X^2\Sigma^+$ ((3)1/2 ← (1)1/2) transition is about 8.5 D over the whole 3.5–20.0 Å region (see Fig. 2), the $2^2\Sigma^+_{1/2}$ ((3) 1/2) state is the best candidate for the optical scheme for the formation of RbYb molecules in the ground rovibronic state [4].

4. Conclusions

We have calculated the potential energy curves for the ground and twelve low-lying excited states of the RbYb molecule at the CASSCF(3,18)/XMCQDPT2 + SOC level of theory. We have predicted the molecular spectroscopic constants and other characteristics for all of the above-mentioned states. Since at the Rb(5p) + Yb(6s^2) dissociation limit our calculated PECs are in a good agreement with the experimental [15] energies and since our earlier calculations for the KRb molecule [12] in a similar approximation predict the spectroscopic parameters of the ground state of the KRb molecule with a high accuracy, we assume that the results of our calculations for the ground and low-lying excited states of the RbYb molecule are also close to the realistic values. The obtained data seem useful for spectral experiments with RbYb molecules.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2017.01.008.

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