

Simulation of optical cycles and spectral-energetic characteristics of electronic states for RbYb and CsYb molecules



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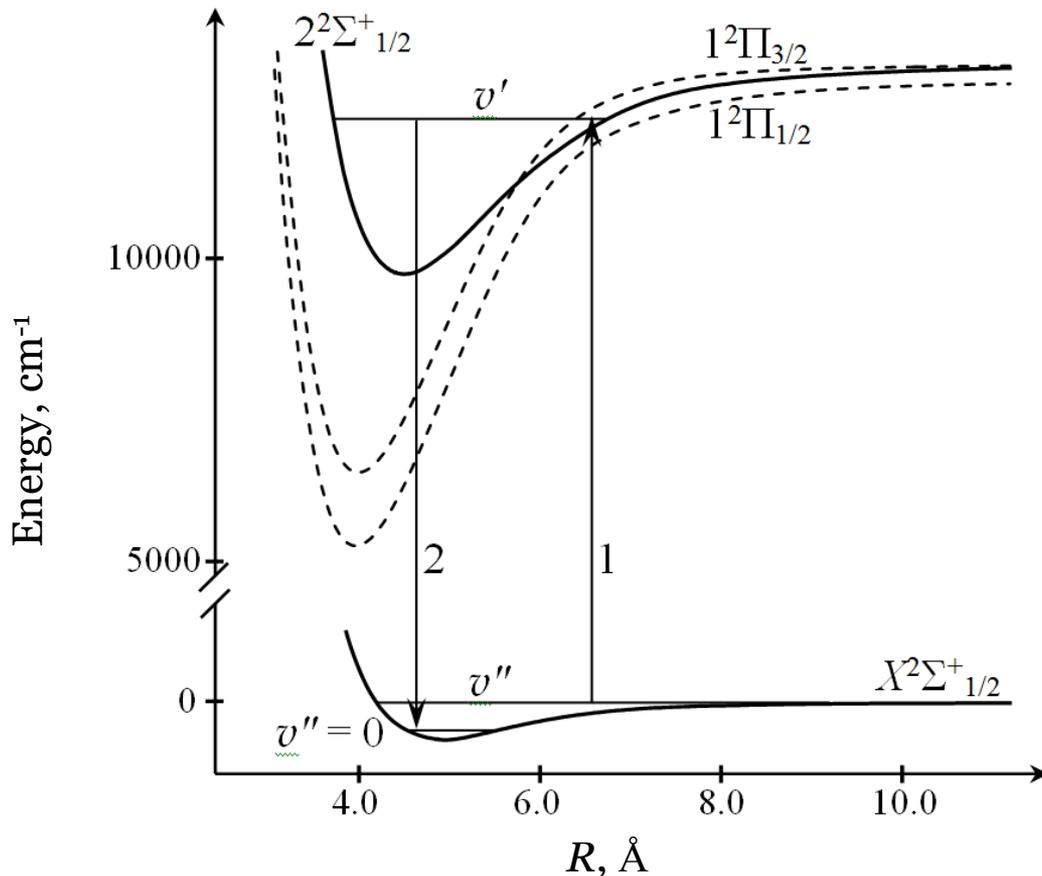
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Cold and ultracold polar diatomic molecules



- One of the modern areas of chemical physics is studying and obtaining a new form of matter – the Bose-Einstein condensate. For the first time this form of matter was synthesized in gases of alkali metals at ultralow temperatures.
- Unlike atoms molecules have more complex structure and possess additional degrees of freedom.
- Stable ensembles of polar molecules with a significant permanent electric or magnetic dipole moment can be manipulated by electric or magnetic fields.
- Due to the structure and chemical properties cold and ultracold polar diatomic molecules comprising atoms of various alkali metals (KRb, KCs, RbCs, etc.) or an alkali metal and transition metal atom (YbRb, YbCs) is supposed to be used in the development of quantum computers, for testing the fundamental theory of the electric dipole moment of an electron, controlled chemical reactions, etc.
- For the above mentioned purposes, it is necessary to obtain polar diatomic molecules in the ground (so-called "absolute") rovibronic state ($v = 0, J = 0$).

Simulation of optical cycles $X(v'', J'' = 0) \rightarrow E(v', J' = 1) \rightarrow X(v'' = 0, J'' = 0)$



Scheme of the optical cycle involving the ground $X^2\Sigma^+_{1/2}$ and excited $2^2\Sigma^+_{1/2}$ states for RbYb molecule:
 1 – excitation (pump), 2 – stimulated transition (dump)

Method of calculation

The total probability of the optical cycle P is proportional to the product of the probability $P_{X \rightarrow E}^{v'', J'' \rightarrow v', J'}$ optical excitation $X(v'', J'') \rightarrow E(v', J')$ and the probability $P_{E \rightarrow X}^{v', J' \rightarrow v''=0, J''=0}$ of transition to the ground state $E(v', J') \rightarrow X(v''=0, J''=0)$ (here we consider the transitions with selection rules $\Delta J = \pm 1$):

$$P \sim P_{X \rightarrow E}^{v'', J'' \rightarrow v', J'} P_{E \rightarrow X}^{v', J' \rightarrow v''=0, J''=0}$$

Where $P_{E \leftrightarrow X}^{v', J' \leftrightarrow v'', J''} \sim \left| E_E^{v', J'} - E_X^{v'', J''} \right| S_{E \leftrightarrow X} q^{v'v''} S^{JJ''}$; $E_E^{v', J'}$ and $E_X^{v'', J''}$ – energies of rovibronic states; $S_{E \leftrightarrow X}$ – oscillator strength; $q^{v'v''}$ – Franck–Condon factors (FCF); $S^{JJ''}$ – the Hönl–London factors.

Thus, in order to calculate the total probabilities of the optical cycle, it is necessary to know the exact potential energy curves (PEC) of the combining electronic states, the spectral-energetic and dynamic characteristics of their vibrational-rotational subsystems.

RbYb

- Experimental data about the system of electronic states of the RbYb molecule are not available. As a result of the experiments, only values for several vibrational states near the dissociation limit for $1^2\Pi_{1/2}$ and $X^2\Sigma^+_{1/2}$ were obtained.
- Several non-empirical calculations of PEC of ground state were performed in various multiconfiguration approximations. Nevertheless, the calculated values of D_e differ by several times.
 - $R_e = 5.41 \text{ \AA}$ $D_e = 193 \text{ cm}^{-1}$ (Meyer and Bohn¹, MRCI)
 - $R_e = 4.857 \text{ \AA}$ $D_e = 531 \text{ cm}^{-1}$ (Shundalau and Minko, XMCQDPT2)
 - $R_e = 4.909 \text{ \AA}$ $D_e = 565 \text{ cm}^{-1}$ (Shao et al², MRCI),
 - $R_e = 4.89\text{--}4.67 \text{ \AA}$ $D_e = 591\text{--}868 \text{ cm}^{-1}$ (Sørensen et al³, MRCI and CCSD),
 - $R_e = 4.91 \text{ \AA}$ $D_e = 656 \text{ cm}^{-1}$ (Brue and Hutson⁴, CCSD(T))
 - $R_e = 4.99889 \text{ \AA}$ $D_e = \sim 700 \text{ cm}^{-1}$ (Tohme and Korek⁵, MRCI),
 - $R_e = 4.68 \text{ и } 4.77 \text{ \AA}$ $D_e = 704 \text{ и } 786 \text{ cm}^{-1}$ (Borkowski et al⁶, CCSD(T))

¹ E.R. Meyer, J.L. Bohn. Phys. Rev. A 80, 042508 (2009).

² Q. Shao, L. Deng, X. Xing, D. Gou, X. Kuang, H. J. Phys. Chem. A 121, 2187 (2017).

³ L.K. Sørensen, S. Knecht, T. Fleig, C.M. Marian. J. Phys. Chem. A 113, 12607 (2009).

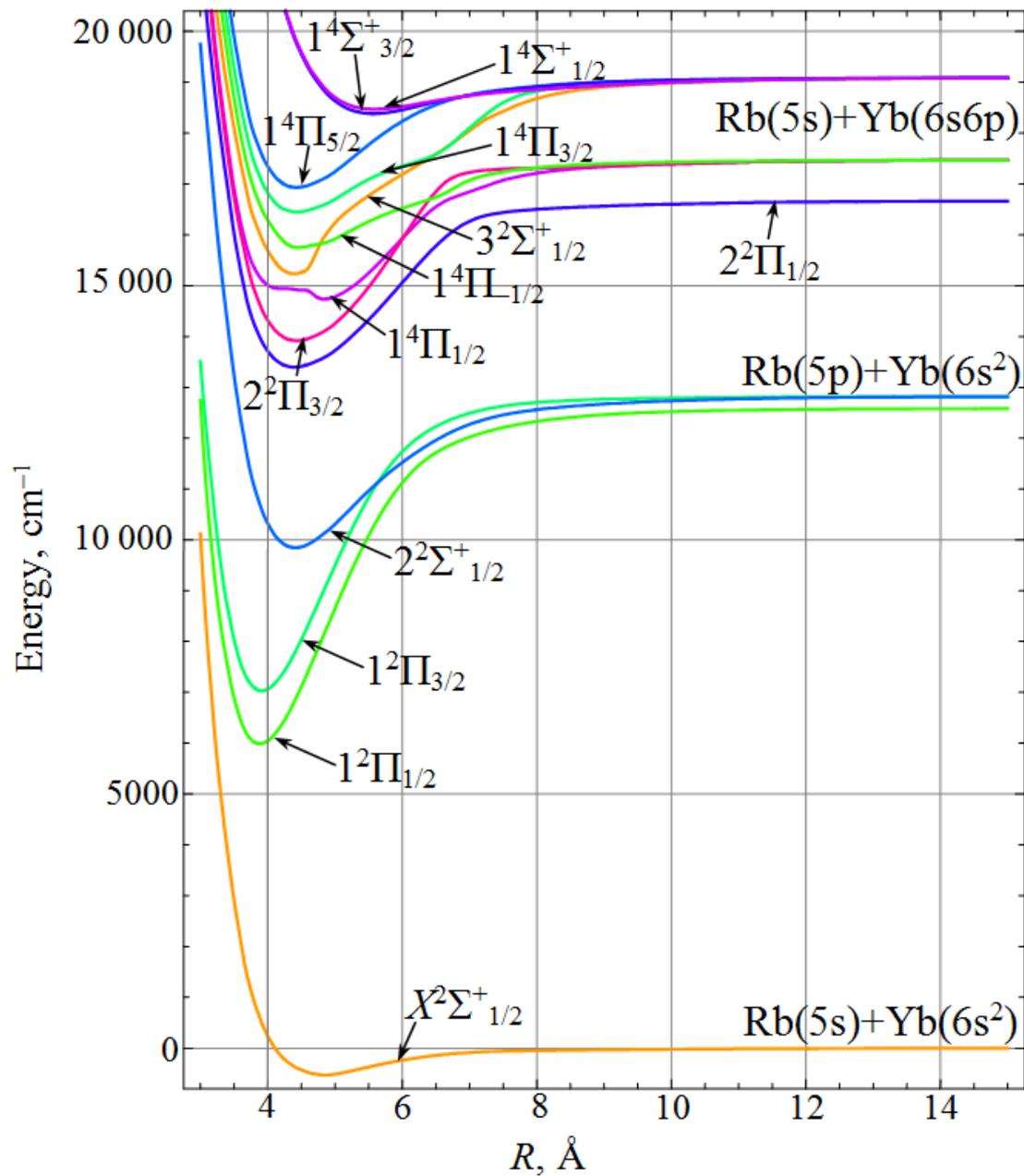
⁴ D.A. Brue, J.M. Hutson. Phys. Rev. A 87, 052709 (2013).

⁵ S.N. Tohme, M. Korek. Chem. Phys. 410, 37 (2013).

⁶ M. Borkowski, P.S. Żuchowski, R. Ciuryło, P.S. Julienne, D. Kędziera, Ł. Mentel, P. Tecmer, F. Münchow, C. Bruni, A. Görlitz. Phys. Rev. A 88, 052708 (2013).

RbYb

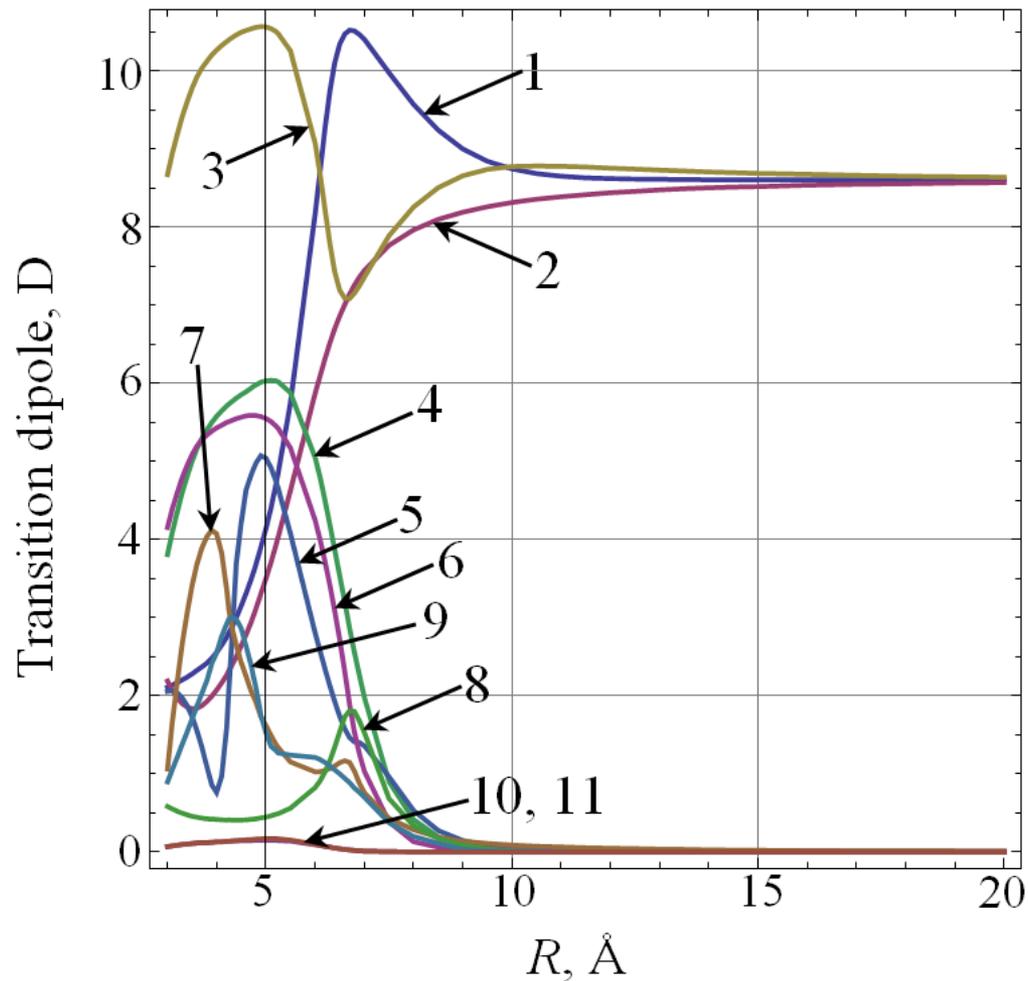
- Basic set:
Stuttgart RSC 60MWB for Yb, Stuttgart RSC ECP28 for Rb
- CASSCF(3,18) with SA procedure, comprising 8 doublet и 3 quartet states
- SA-CASSCF(3,18) calculations are performed pointwisely by step of 0.05 Å for the internuclear distances ranging 3 – 20 Å
- XMCQDPT (Extended Multi-Configuration Quasi-Degenerate Perturbation Theory) (Granovsky, 2011)
- Calculation of the spin-orbit coupling in the one-electron approximation



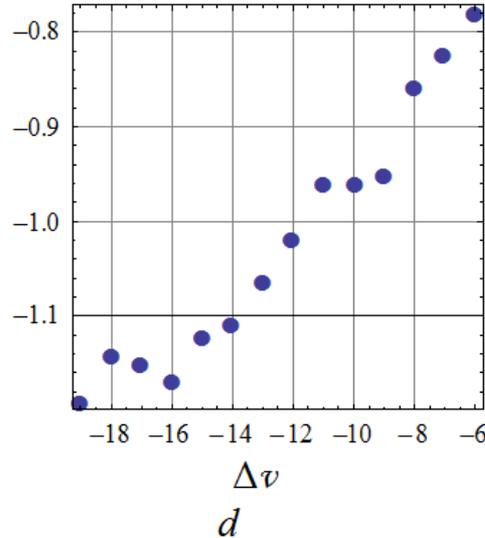
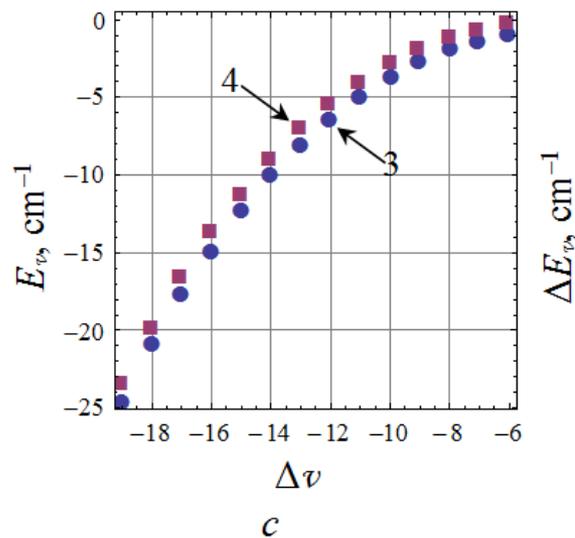
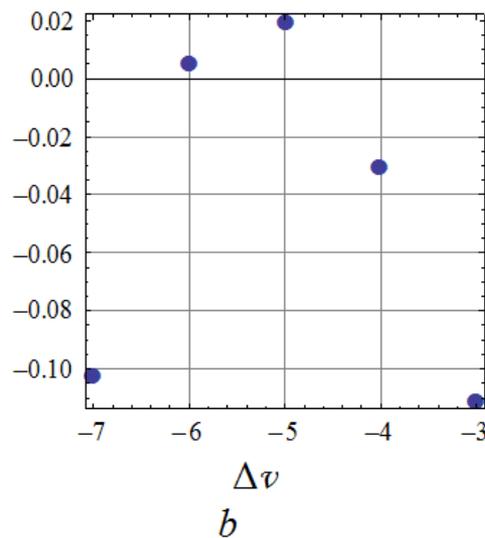
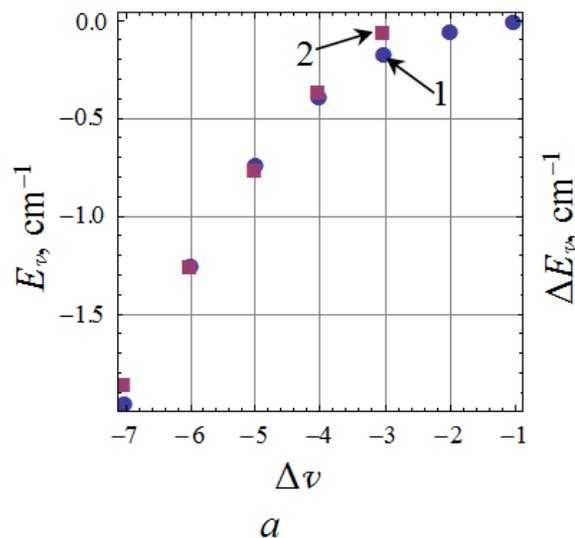
Terms of RbYb in
 SA-CASSCF(3,18)/
 XMCQDPT2 + SOC
 approximation

Asymptotics for YbRb

	Experiment	Calculation
Dissociation limit Yb(6s ²) + Rb(5s)		
Energy of states	0.0	0.0
Dissociation limit Yb(6s ²) + Rb(5p)		
Energy of states	12 578.9	12 614.5
	12 816.5	12 852.6
SOC splitting	237.6	238.1
Dissociation limit Yb(6s6p) + Rb(5s)		
Energy of states	17 288.5	16 929.5
	17 992.0	17 642.7
	19 710.4	19 059.8
SOC splitting	703.5	713.2
	1 718.4	1 417.1



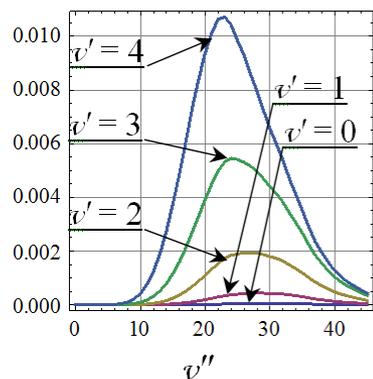
The calculated dipole transition moments between the ground $(1)1/2$ state and states $(2)1/2$ (1), $(1)3/2$ (2), $(3)1/2$ (3), $(4)1/2$ (4), $(5)1/2$ (5), $(2)3/2$ (6), $(1)-1/2$ (7), $(3)3/2$ (8), $(6)1/2$ (9), $(7)1/2$ (10) and $(4)3/2$ (11).



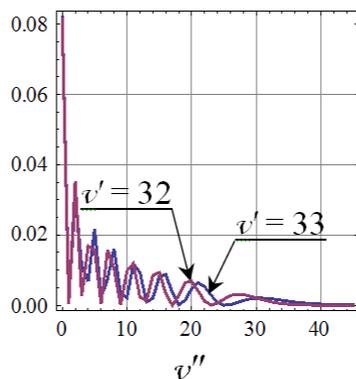
Vibrational energies E_v (a , c), vibrational energy difference $\Delta E_v = E_v(\text{exper}) - E_v(\text{calc})$ (b , d) for the ground $X^2\Sigma^+_{1/2}$ (a , b) and first excited $1^2\Pi_{1/2}$ (c , d) states $^{87}\text{Rb}^{176}\text{Yb}$ molecule: (1) Münchow et al.¹, (3) Nemitz et al.², (2) and (4) our calculations.

¹F. Münchow, C. Bruni, M. Madalinski, A. Görlitz, Two-photon photoassociation spectroscopy of heteronuclear YbRb, Phys. Chem. Chem. Phys. 13 (2011) 18734–18737.

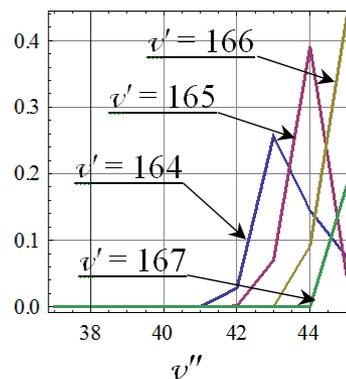
²N. Nemitz, F. Baumer, F. Münchow, S. Tassy, A. Görlitz, Production of heteronuclear molecules in an electronically excited state by photoassociation in a mixture of ultracold Yb and Rb, Phys. Rev. A, 79 (2009) 061403.



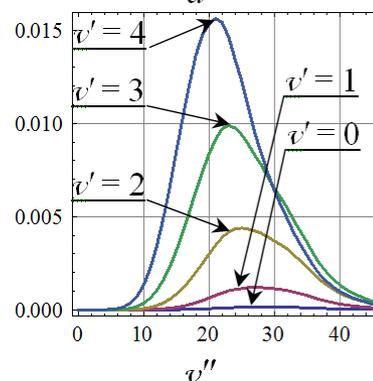
a



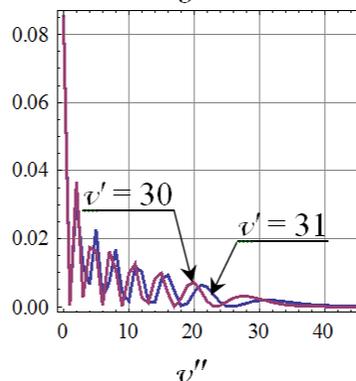
b



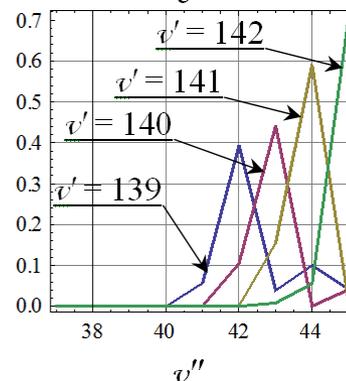
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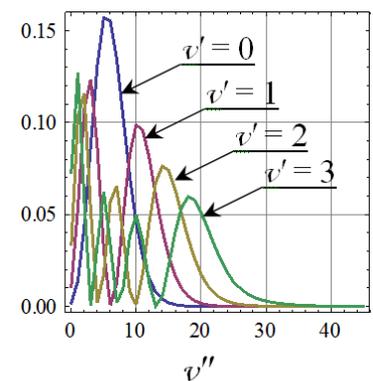
d



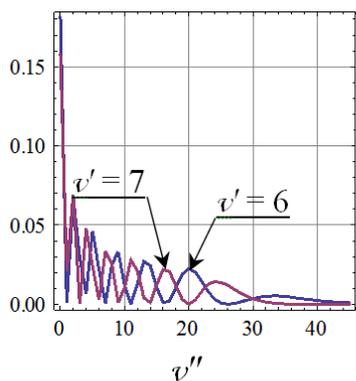
e



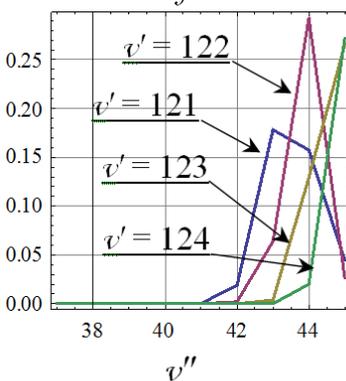
f



g



h



i

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

CsYb

- Experimental data about the system of electronic states of the YbCs molecule are not available.
- 3 non-empirical calculations of PEC of ground state were performed in multiconfiguration coupled cluster approximation. Nevertheless the calculated values of D_e differ by 3 times.
- For the ground state:
 - $R_e = 5.657 \text{ \AA}$ $D_e = 182.0 \text{ cm}^{-1}$ (E.R. Meyer, J.L. Bohn.¹)
 - $R_e = 5.763 \text{ \AA}$ $D_e = 158.6 \text{ cm}^{-1}$ (D.N. Meniailava, M.B. Shundalau)
 - $R_e = 5.144 \text{ \AA}$ $D_e = 621.1 \text{ cm}^{-1}$ (D.A. Brue, J.M. Hutson.²)
 - $R_e = 5.161 \text{ \AA}$, $D_e = 542 \text{ cm}^{-1}$ (Q. Shao et al.³)

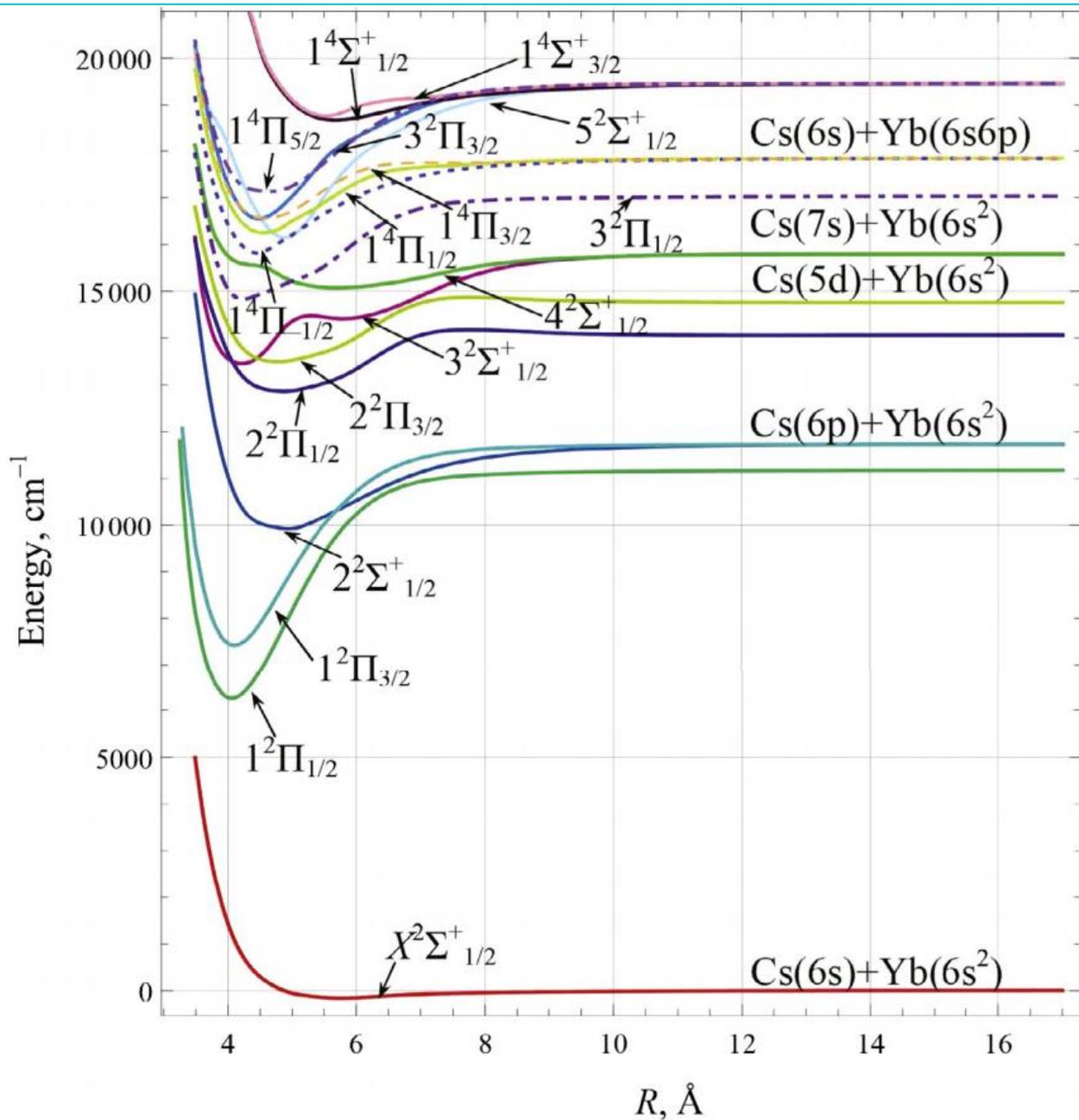
¹ E.R. Meyer, J.L. Bohn. Phys. Rev. A 80, 042508 (2009)

² D.A. Brue, J.M. Hutson. Phys. Rev. A 87, 052709 (2013)

³ Q. Shao, L. Deng, X. Xing, D. Gou, X. Kuang, H. J. Phys. Chem. A 121, 2187 (2017).

CsYb

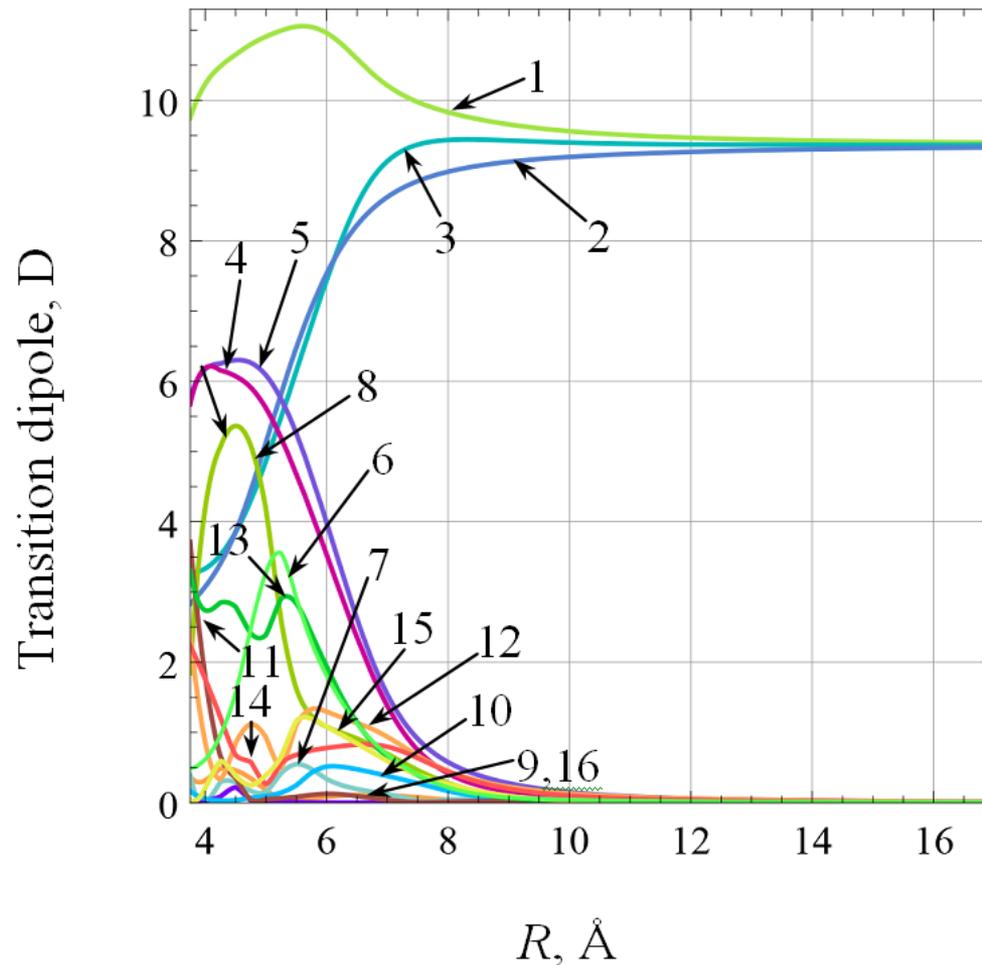
- Basis set:
Stuttgart RSC ECP60MDF for Yb, Stuttgart RSC ECP49MDF for Cs
- CASSCF(3,12) with SA procedure, comprising 11 doublet и 3 quartet states
- SA-CASSCF(3,12) calculations are performed pointwisely by step of 0.01 Å for the internuclear distances ranging 3.8 – 17 Å
- XMCQDPT (Extended Multi-Configuration Quasi-Degenerate Perturbation Theory) (Granovsky, 2011)
- Calculation of the spin-orbit coupling in the one-electron approximation



Terms of CsYb in
SA-CASSCF(3,12)/
XMCQDPT2 + SOC
approximation

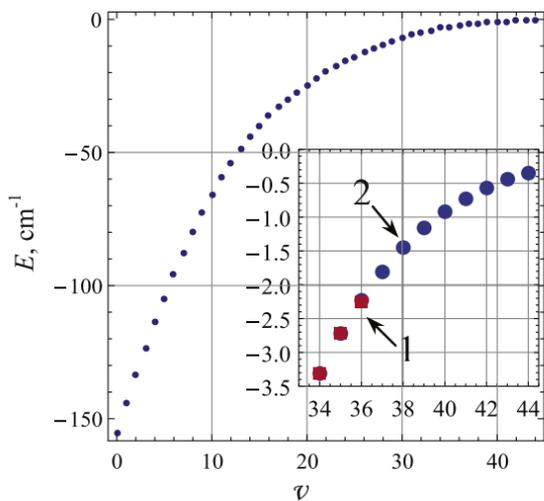
Asymptotics for CsYb

	Experiment	Calculation
Dissociation limit Yb(6s ²) + Cs(6s)		
Energy of states	0.0	0.0
Dissociation limit Yb(6s ²) + Cs(6p)		
Energy of states	11 178.0	11 178.0
	11 728.9	11 732.3
SOC splitting	550.9	554.3
Dissociation limit Yb(6s ²) + Cs(5d)		
Energy of states	14 499.3	14 063.3
	14 596.8	15 794.6
SOC splitting	97.5	1 731.3
Dissociation limit Yb(6s ²) + Cs(7s)		
Energy of states	18 535.5	15 795.7
Dissociation limit Yb(6s6p) + Cs(6s)		
	17 288.5	17 034.9
Energy of states	17 992.0	17 841.4
	19 710.4	19 457.4
SOC splitting	2 421.9	2 422.5

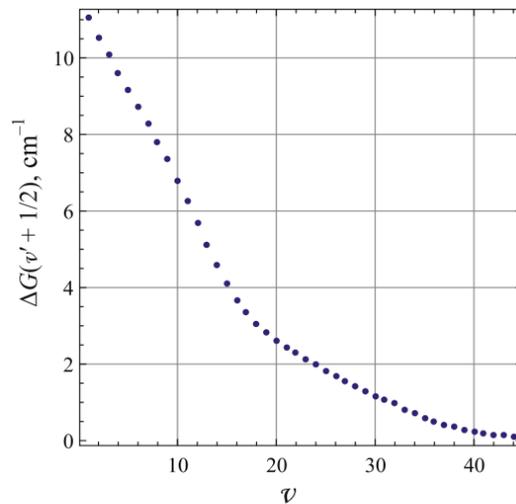


The calculated dipole transition moments between the ground $(1)_{1/2}$ state and states $(2)_{1/2}$ (1), $(1)_{3/2}$ (2), $(3)_{1/2}$ (3), $(4)_{1/2}$ (4), $(2)_{3/2}$ (5), $(5)_{1/2}$ (6), $(6)_{1/2}$ (7), $(7)_{1/2}$ (8), $(1)_{-1/2}$ (9), $(8)_{1/2}$ (10), $(3)_{3/2}$ (11), $(9)_{1/2}$ (12), $(4)_{3/2}$ (13), $(10)_{1/2}$ (14), $(5)_{3/2}$ (15) and $(1)_{5/2}$ (16).

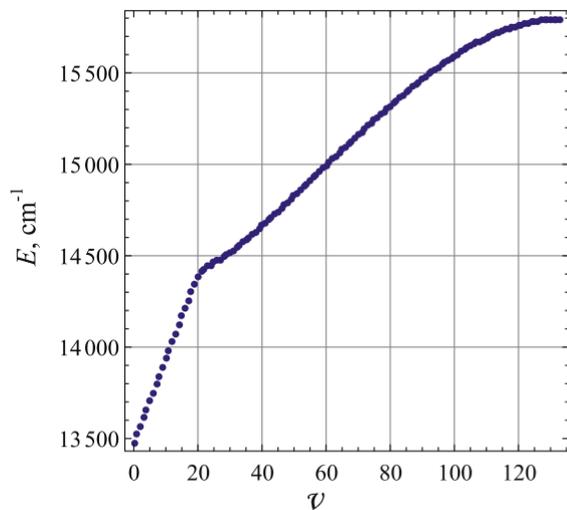
The system of vibrational levels



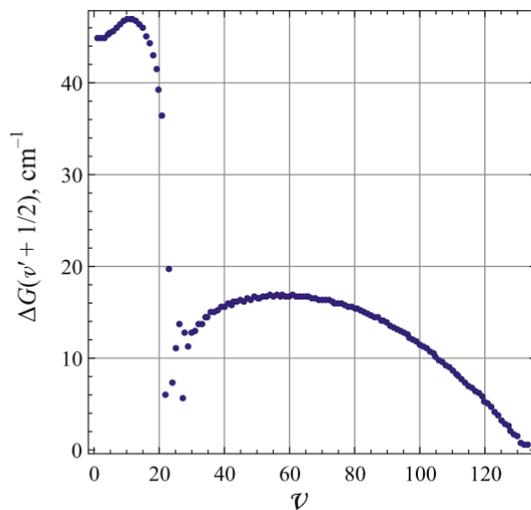
a



b

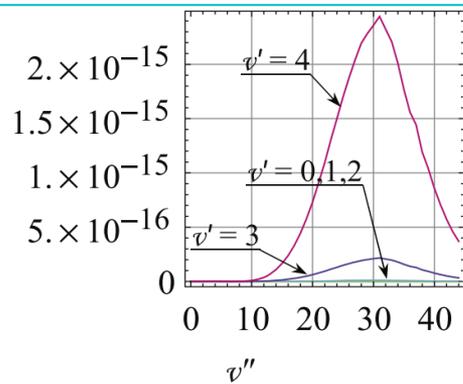


c

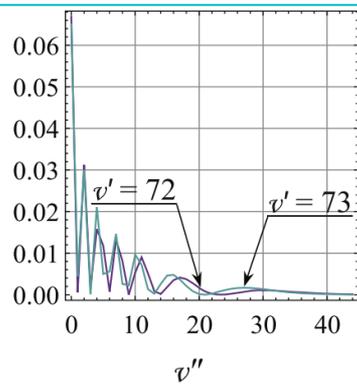


d

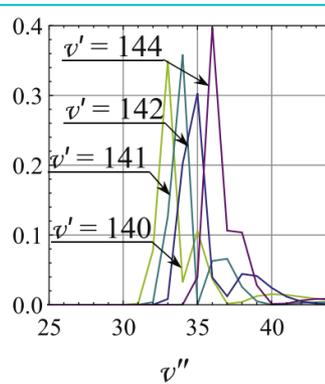
Vibrational energies E_ν (a, c) and vibrational energy difference $\Delta G(\nu' + 1/2)$ (b, d) for the ground $X^2\Sigma^+_{1/2}$ (a, b) and excited $3^2\Sigma^+_{1/2}$ (c, d) states of $^{133}\text{Cs}^{176}\text{Yb}$ molecule. The inset shows sequences of vibrational energies near the dissociation limit, calculated without (1) and with asymptotic function (2).



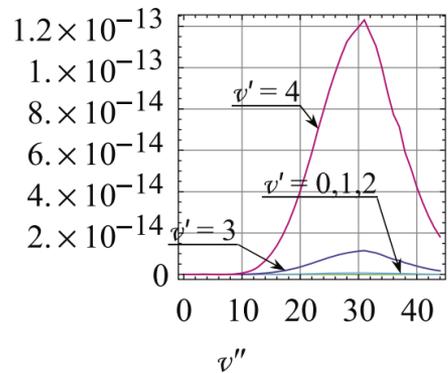
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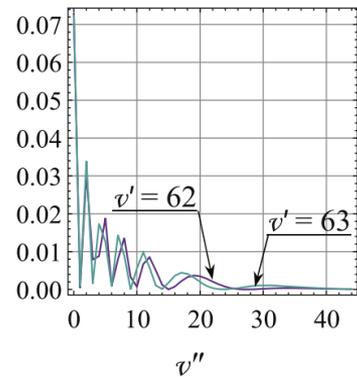
b



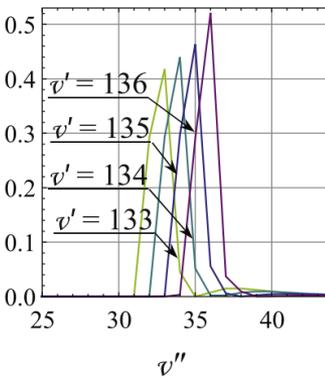
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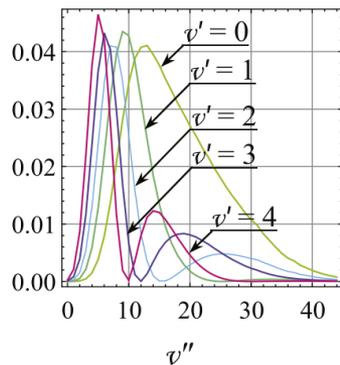
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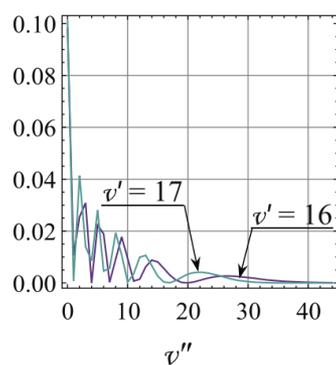
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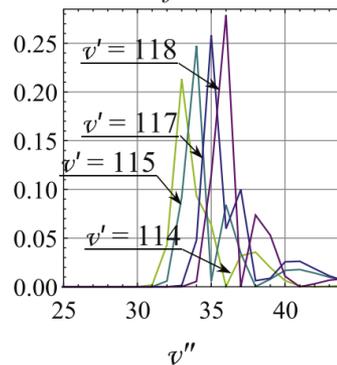
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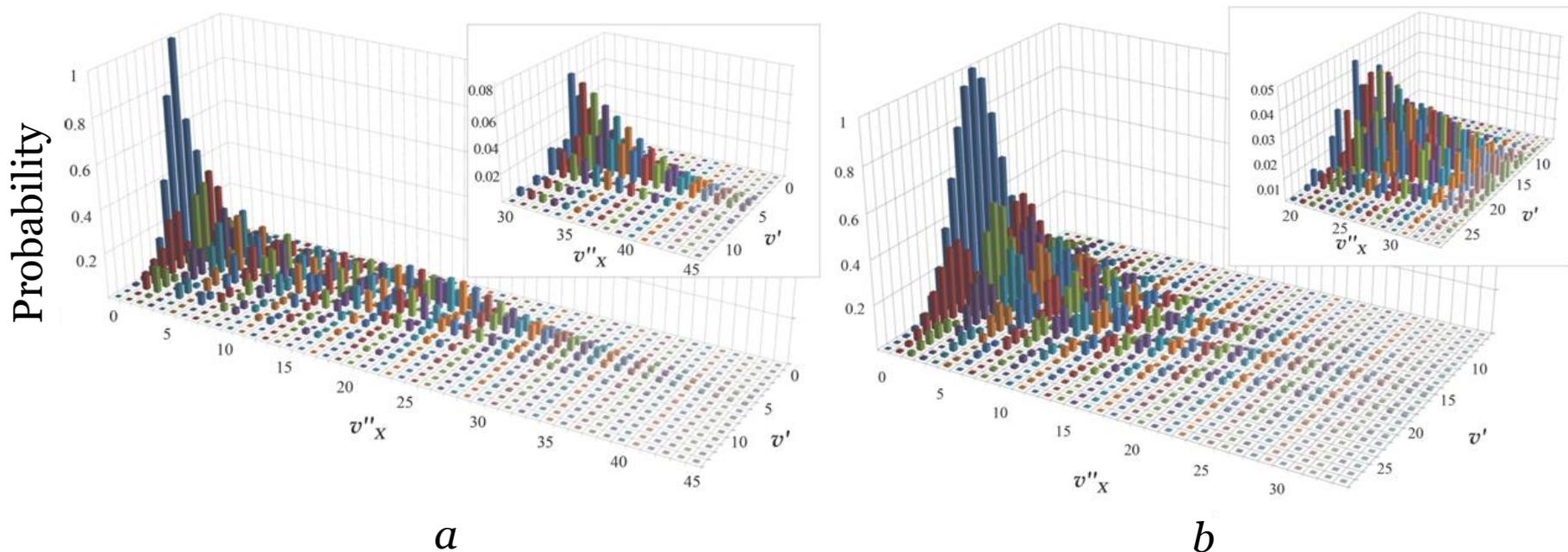
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i

Franck–Condon factors
 for $X^2\Sigma^+_{1/2} \leftarrow 1^2\Pi_{1/2}$
 transitions (a–c),
 for $X^2\Sigma^+_{1/2} \leftarrow 1^2\Pi_{3/2}$
 transitions (d–f)
 and for $X^2\Sigma^+_{1/2} \leftarrow 2^2\Sigma^+_{1/2}$
 transitions (g–i),
 calculated using
 $\Delta J = 0$ selection rules
 for $^{133}\text{Cs}^{176}\text{Yb}$ molecule.

For constructing effective optical cycles for RbYb and CsYb molecules as an upper electronic state, it was expedient to use one of the states ($2^2\Sigma^+_{1/2}$, $1^2\Pi_{3/2}$ or $1^2\Pi_{1/2}$), belonging to the dissociation limit $\text{Rb}(5p) + \text{Yb}(6s^2)$ (or $\text{Cs}(6p) + \text{Yb}(6s^2)$).



The probabilities of optical cycles for RbYb (*a*) and CsYb (*b*) molecules with the participation of excited $2^2\Sigma^+_{1/2}$. The presented probability distributions are normalized to the maximum values, corresponding to transitions $v'' = 0 \rightarrow v' = 6$ for RbYb и $v'' = 0 \rightarrow v' = 17$ for CsYb. Each value of P with coordinates (v'', v') on the diagrams determines the probability of excitation from the vibronic state $X^2\Sigma^+_{1/2}(v'')$ to state $2^2\Sigma^+_{1/2}(v')$ and radiative transition to the state $X^2\Sigma^+_{1/2}(v'' = 0)$.

- Similar diagrams were obtained for optical cycles involving upper electronic states $1^2\Pi_{3/2}$ and $1^2\Pi_{1/2}$.
- Optical cycles with the participation of excited Π -states turn out to be significantly less effective. Differences in the values of the probabilities for optical cycles involving $2^2\Sigma^+_{1/2}$ and Π -states are primarily due to the dipole moments of the corresponding electronic transitions. The average values of the transition dipole moments $X^2\Sigma^+_{1/2} \rightarrow 2^2\Sigma^+_{1/2}$ for RbYb and CsYb molecules are about 8.5 D и 9.2 D, respectively, in a broad (3.5–20 Å) range of internuclear distances, while the transition dipole moments $X^2\Sigma^+_{1/2} \rightarrow 1^2\Pi_{3/2}$ and $X^2\Sigma^+_{1/2} \rightarrow 1^2\Pi_{1/2}$ decrease from 8–9 D in the area of internuclear distances 15–20 Å to 2 D near 4 Å.
- However, the decisive role here is played by the difference in the FCF values, which are 1-2 orders of magnitude smaller for transitions from Π -states than for transitions from the $2^2\Sigma^+_{1/2}$ state.

Conclusions

- Potential energy functions were calculated for the ground and 12 excited states for the RbYb molecule in the CASSCF(3,18) / XMCQDPT2 + SOC approximation ; and for the ground and 16 excited states for the CsYb molecule in the CASSCF(3,12) / XMCQDPT2 + SOC approximation. The values of the energies obtained for Rb(5p)+Yb(6s²) and Cs (6p)+Yb(6s²) dissociation limit, are in agreement with experimental energies.
- Also, molecular constants and other spectral-energy and dynamic characteristics of the obtained electronic states were predicted.
- On their basis, the probabilities of optical cycles for the effective transfer of polar diatomic molecules RbYb and CsYb into an "absolute" rovibronic state with the help of low-lying excited electronic states.
- It is shown that when forming RbYb and CsYb molecules through photoassociation, the most effective two-step schemes for transferring molecules from highly excited vibrational states to the ground state can be realized by the following channels: $X^2\Sigma^+_{1/2}(v'' = 30\dots45) \rightarrow 2^2\Sigma^+_{1/2}(v' = 4\dots8) \rightarrow X^2\Sigma^+_{1/2}(v'' = 0)$ for RbYb molecule and $X^2\Sigma^+_{1/2}(v'' = 19\dots36) \rightarrow 2^2\Sigma^+_{1/2}(v' = 13\dots23) \rightarrow X^2\Sigma^+_{1/2}(v'' = 0)$ for CsYb molecule.

- This work was carried out with partial financial support of the State Committee for Science and Technology of the Republic of Belarus

Thank you for attention