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Theoretical study of highly-excited states of KRb molecule

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Abstract: Semi-empirical adiabatic potential energy curves of highly excited states of the KRb molecule are calculated as a function of the internuclear distance R over a wide range from 3 to 150 a_0. The diatomic molecule is treated as an effective two-electron system by using the large core pseudopotentials and core polarization potentials. All calculations are performed by using the nonrelativistic CASSCF/MRCI method with accurate basis set functions. The spectroscopic constants of the calculated electronic states agree well with experimental data, including the recent ones from Lee *et al.*, and with available theoretical results.

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1. Introduction

Polar alkali molecules, and in particular KRb, have recently been the object of intensive experimental [1–12] and theoretical [13–16] studies. For instance, the KRb molecule often serves as an example of a reactive species in order to explain the collision rates of trapped and ultracold polar molecules (*e.g.* [17–19]), as well as spectra observation under cold conditions (*e.g.* [20]). Recently, Stwalley *et al.* [21] analyzed pathways for direct photoassociative formation of ultracold heteronuclear alkali metal dimers including KRb. Moreover, the very recent experimental investigations of Lee *et al.* [11, 12] provide a valuable opportunity to test the accuracy of our computational methods applied to highly excited states.

Highly lying theoretical energy curves correlated up to the limit K(*3d*) + Rb(*5s*) were given by Yiannopoulou *et al.* [13]. They performed extensive configuration interaction (CI) calculations using, amongst other tools, the MOLCAS program [22]. Two types of calculations were made: the first with a small relativistic core and the second including all electrons. Rousseau *et al.* [14] used the package CIPSI [23, 24] (Configuration Interaction by Perturbation of a multiconfiguration wave function Selected Iteratively) to preform CI calculations up to the K(*4s*) + Rb(*4d*) asymptotic limit. Here, both atoms were treated as effective one-electron systems. Park *et al.* [15] used the

MOPLRO 1999 program package[1] employing the small core pseudopotentials with appropriate core polarization potentials (CPP) and went to the very high asymptotic limit of K($5s$) + Rb($5d$).

This paper presents results of semi-empirical nonrelativistic calculations on highly excited states of the KRb molecule. Our present calculations are based on the complete active space self-consistent-field/multi-reference configuration interaction (CASSCF/MRCI) scheme. In contrast to the Park's *et al.* [15] approach we have decided to use large core pseudopotentials, which has led us to an effective two electron calculation. Additionally, a different set of basis functions is employed in our calculation. The basis set for K consists of the ECP18SDF pseudopotential base augmented by twenty-eight s and five p functions, with d and f functions described by the ECP10MDF pseudopotential augmented by six d and five f functions. The second basis set for Rb consists of the ECP36SDF pseudopotential basis set augmented by twelve s and five p functions, the d and f functions are taken from the ECP28MDF pseudopotential basis sets augmented by six d and two f functions. The present calculation also uses the electron core polarization potential, which enables us to provide high accuracy of highly-lying adiabatic potential curves. The accuracy of the obtained adiabatic curves are estimated by comparison with the only available, recent experimental data of Lee *et al.* [11] and with the theoretical results coming from extensive *ab initio* calculations of Yiannopoulou *et al.* [13], Rousseau *et al.* [14] and Park *et al.* [15]. This description of the KRb system aims to help design some details of possible photodissociation and photoassociation experiments.

Section 2 briefly describes the computational method, then Section 3 presents the results and discusses their comparison with available experimental data and theoretical results. Finally, in the last section, summary and conclusions are provided.

2. Computational method

A detailed description of the computational method is given in our earlier papers [25, 26] and is based on the description given by Czuchaj *et al.* [27]. Therefore this section only summarizes the main aspects of the theory.

We consider the interaction between two alkali atoms. Let R be the separation between the nuclei of these atoms. We seek for the solutions of the Schrödinger equation within the Born-Oppenheimer approximation. In the present approach only the valence electrons are treated explicitly, but the atomic cores are represented by l-dependent pseudopotentials. The total Hamiltonian of the considered system can be written as

$$H = T + V, \tag{1}$$

where T stands for the kinetic energy operator of the valence electrons and V represents the interaction operator. The latter is put into the form

$$V = \sum_{\lambda}\left(V^{\lambda} + V^{\lambda}_{pol}\right) + \sum_{j>i=1}^{N}\frac{1}{r_{ij}} + V_{cc}, \tag{2}$$

where the index λ goes over the atomic cores of atoms A and B. Here, A corresponds to potassium and B to rubidium. V^{λ} describes the Coulomb and exchange interaction as well as the Pauli repulsion between the valence electrons and the core λ and is defined as

$$V^{\lambda} = \sum_{i=1}^{N}\left(-\frac{Q_{\lambda}}{r_{\lambda i}} + \sum_{l,k} B^{\lambda}_{l,k}\exp\left(-\beta^{\lambda}_{l,k} r^{2}_{\lambda i}\right) P^{\lambda}_{l}\right), \tag{3}$$

where Q_{λ} denotes the net charge of the core λ, P^{λ}_{l} is the projection operator onto the Hilbert subspace of angular symmetry l with respect to core λ and N is the number of the valence electrons. The parameters $B^{\lambda}_{l,k}$ and $\beta^{\lambda}_{l,k}$ define the semi-local energy-consistent pseudopotentials. The second interaction term in Eq. (2) is the polarization term which describes, amongst others, core-valence correlation effects [20] and, in the case of atom A, is taken as

$$V^{A}_{pol} = -\frac{1}{2}\alpha_{A}\mathbf{F}^{2}_{A}, \tag{4}$$

where $\alpha_{A} = 5.354\ a^{3}_{0}$ [28] is the dipole polarizability of the A^{+} core and $\mathbf{F}_{A}$ is the electric field generated at its site by the valence electrons and the other core. In the case of the second atom B, $\alpha_{B} = 8.67\ a^{3}_{0}$ [29]. The electric field can be written as

$$\begin{aligned}\mathbf{F}_{A} = {} & \sum_{i}\frac{\mathbf{r}_{Ai}}{r^{3}_{Ai}}\left[1 - \exp\left(-\delta_{A} r^{2}_{Ai}\right)\right] + \\ & - \frac{Q_{B}\mathbf{R}}{R^{3}}\left[1 - \exp\left(-\delta_{A} R^{2}\right)\right], \end{aligned} \tag{5}$$

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[1] MOLPRO is an *ab initio* program package written by H.J. Werner and P.J. Knowles with contributions from J. Almlöf, R.D. Amos, A. Berning, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, P. Palmieri, K.A. Peterson, R.M. Pitzer, H. Stoll, A.J. Stone, and P.R. Taylor, 1999.

where for K $\delta_A = 0.29\ a_0^{-2}$ [28] is the cutoff parameter. For Rb $\delta_B = 0.23\ a_0^{-2}$ [29]. The third term in Eq. (2) represents the Coulomb repulsion between the valence electrons, whereas the last term describes the core-core interaction. Since the alkali atomic cores are well separated, a simple point-charge Coulomb interaction was chosen in the latter case.

All calculations reported in this paper were performed by means of the MOLPRO program package[2]. The core electrons of K atoms were represented by the pseudopotential ECP18SDF [28]. Additionally, this basis set was augmented by twenty eight *s* functions (1420.669249, 1285.100176, 616.034056, 76.345701, 42.76875, 39.898077, 26.791999, 18.608373, 11.270336, 10.513862, 4.535573, 3.412686, 1.618743, 0.577728, 0.465037, 0.213265, 0.097803, 0.065676, 0.035499, 0.009433, 0.005909, 0.004326, 0.001984, 0.00157, 0.000923, 0.000532, 0.000232, 0.00006) and five *p* functions (17.126069, 4.012627, 0.940156, 0.004358, 0.001929). Here, the numbers in parenthesis are coefficients of the exponents of the primitive gaussian orbitals. In the case of *d* and *f* orbitals, instead of using the remaining part of the basis set which formed this pseudopotential we used the equivalent part of the another one, much richer basis set which comes with ECP10MDF pseudopotential [29]. Moreover, it was augmented by six *d* functions (25.549602, 10.052166, 3.954897, 0.010789, 0.003932, 0,001433) and two *f* functions (1.680236, 0.029604). Similarly, for Rb, the core electrons are represented by the pseudopotential ECP36SDF [30, 31]. This basis set was augmented by twelve *s* functions (78.792874, 33.933628, 15.970335, 12.94337, 4.937015, 1.883135, 0.104504, 0.068519, 0.007182, 0.001597, 0.000355, 0.000188) and five *p* functions (5.258465 1.648345 0.516699 0.004459 0.002001). Again, in the case of *d* and *f* orbitals, the appropriate part of the basis set was taken from another pseudopotential, namely ECP28MDF [29]. We augmented this part of the basis by adding six *d* functions (2.425571, 1.716379, 1.214541, 0.009151, 0.003285, 0.00118) and finally two *f* functions (8.194323, 0.061857). All basis functions were checked in order to ensure linear independence.

The quality of our basis set was checked by performing CI calculations for the ground and several excited states of the isolated potassium and rubidium atoms. Additionally, we slightly adjusted the cutoff parameters δ_A and δ_B in the effective core-polarization potentials to better reproduce experimental atomic energies. The change of the cutoff parameters does not exceed 7%. The calculated KRb adiabatic potentials correlate to the K(4*s*) + Rb(4*d*), K(4*s*) + Rb(6*s*) and K(5*s*) + Rb(5*s*) excited atomic asymptotes. The comparison of experimental [1] and theoretical [14, 16] asymptotic energies for different states is shown in Tab. 1. We note very good agreement between our atomic energies and the experimental ones given by Moore [1]. The potential energy curves for KRb are calculated using the complete-active-space self-consistent-field (CASSCF) method to generate the orbitals for the subsequent CI calculations. The corresponding active space in the C_{2v} point group involved the molecular counterparts of the 4*s*, 4*p*, 5*s*, 3*d* and 5*p* valence orbitals of the K atom and 5*s*, 5*p*, 4*d*, 6*s*, 6*p* and 5*d* valence orbitals of the Rb atom.

3. Results and discussion

Calculations of the adiabatic energy curves were performed for the internuclear separation *R* in the range from 3 a_0 up to 150 a_0. Numerical values of the calculated potential energies are shown in Tab. 2. Our results are also plotted in Fig. 1 and 2 in the range up to 40 a_0 and compared with the potential curves of Rousseau *et al.* [14]. All of our potential curves generally lie below the Rousseau ones and this is particularly clear in the vicinity of the potential wells (see Fig. 1). In addition, there is good agreement in shapes, which is also noticeable in the cases of the unusual shapes displayed by the $4^1\Sigma^+$, $5^1\Sigma^+$ and $3^3\Pi$ states (Fig. 1 and 2). It is visible that the $4^1\Sigma^+$ and $5^1\Sigma^+$ curves avoid crossing each other at the internuclear distances *R* at around 8 and 13 a_0 leading to irregularities in vibronic spectra [11]. Also, the well pronounced avoided crossing between $5^1\Sigma^+$ and $6^1\Sigma^+$ takes place at around 21 a_0, where our $5^1\Sigma^+$ potential curve displays a small maximum.

Equilibrium positions R_e, depths of the potential wells D_e and electronic energy terms T_e were obtained using cubic spline approximation to the calculated potentials around their equilibrium positions. The spectroscopic parameter ω_e was calculated by solving the Schrödinger equation with the calculated adiabatic potentials. The values of

[2] MOLPRO, version 2006.1, a package of *ab initio* programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, see http://www.molpro.net.

Table 1. Asymptotic energies (cm^{-1}): comparison with other calculations and experiments.

	Present work	Moore [1]	Leininger *et al.* [16]	Rousseau *et al.* [14]
K(4s) + Rb(4d)	19355	19355	19366	19354
K(4s) + Rb(6s)	20132	20134	20134	20101
K(5s) + Rb(5s)	21034	21027	21025	21018

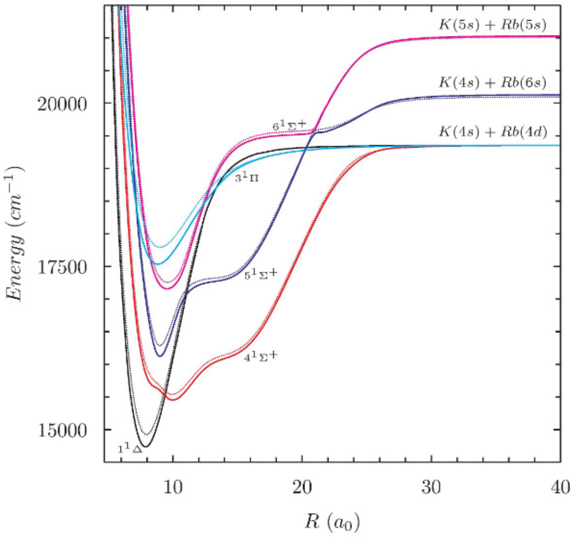

Figure 1. Comparison of the singlet excited molecular states correlating to the K(4s) + Rb(4d), K(4s) + Rb(6s) and K(5s) + Rb(5s) asymptotes with the theoretical results of Rousseau *et al.* [14] (dotted lines).

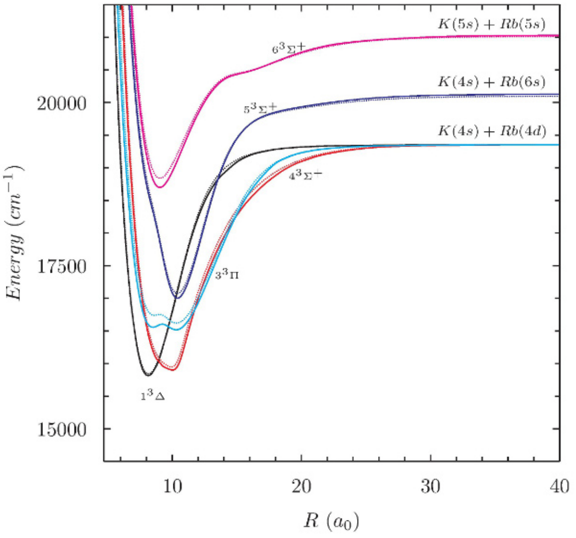

Figure 2. Comparison of the triplet excited molecular states correlating to the K(4s) + Rb(4d), K(4s) + Rb(6s) and K(5s) + Rb(5s) asymptotes with the theoretical results of Rousseau *et al.* [14] (dotted lines).

the molecular constants are shown in Tab. 3. Generally, a consistent agreement can be seen between our results and the recent theoretical ones of Rousseau *et al.* [14] and Park *et al.* [15]. More interestingly is the comparison with existing experimental data. Indeed, for the $5^1\Sigma^+$ state and the case of T_e constant the best agreement with the recent experiment of Lee *et al.* [11] is shown by Rousseau *et al.* [14]. Our result with $\Delta T_e = 41$ cm^{-1} lies in reasonable vicinity, while the result of Yiannopulou at al. [13] gives a larger discrepancy ($\Delta T_e = 56$ cm^{-1}).

It is also possible to compare with the data of Lee at al. [11] for the $1^3\Delta$ state, where in the case of T_e the results of Yiannopoulou *et al.* [13] and Rousseau *et al.* [14] lie within the range of 88 cm^{-1}, while ours and Parks *et al.* [15] results are just outside 250 cm^{-1}. For ω_e all the theoretical results show good agreement with each other, with the slight exception of Yiannopoulou *et al.* The last set of experimental data comes from the older (2001) paper of Lee *et al.* [32], it includes the values of R_e, T_e and ω_e for the $1^1\Delta$ state. Our calculations give very good agreement with $\Delta R_e = 0.03$ a_0. For T_e, our results and those of Rousseau *et al.* show the best agreement with experimental data. Again, for ω_e, all theoretical results, with the exception of Yiannapoulou *et al.*, display good agreement with the experimental value.

Using our calculations of potential energy curves we give an example (see Fig. 3) of a possible pathway for photoassociative formation of KRb in excited rovibrational levels of its ground electronic state $X^1\Sigma^+$. We propose one photon or two photon excitation of total energy 19354 cm^{-1} just at the K(4s) + Rb(4d) atomic asymptote. Although, direct pumping due to forbidden atomic electric dipole transition is expected to be very weak, still the formation of the ground electronic state in some rovibrational levels can be achieved by a spontaneous emission because the molecular electric dipole transition is allowed.

Table 2. Adiabatic potential energy curves of the KRb molecule for $4-6^1\Sigma^+$, $4-6^3\Sigma^+$, $3^1\Pi$, $3^3\Pi$, $1^1\Delta$ and $1^3\Delta$ states. Energies are shown in cm^{-1} units.

$R(a_0)$	$4^1\Sigma^+$	$5^1\Sigma^+$	$6^1\Sigma^+$	$4^3\Sigma^+$	$5^3\Sigma^+$	$6^3\Sigma^+$	$3^1\Pi$	$3^3\Pi$	$1^1\Delta$	$1^3\Delta$
3.00	350581.20	352099.01	354846.11	345424.04	347355.88	349059.88	339758.15	339764.68	335581.54	332178.54
3.20	242514.89	245113.05	246282.76	245239.59	246153.43	247266.18	241736.63	242091.71	237661.26	234668.53
3.40	171049.95	174283.54	174510.29	172191.08	172848.98	173427.09	169767.20	170338.56	166011.33	163511.11
3.60	123818.49	126625.89	126911.21	126041.25	127395.54	127734.64	120919.72	121656.21	117469.65	115571.88
3.80	91931.71	94759.56	95103.56	93865.33	94812.38	95568.56	88583.64	89474.54	85561.29	84119.58
4.00	69635.81	73320.98	73365.39	72387.36	73423.10	74264.40	67073.71	68074.99	64039.06	63355.49
4.20	54600.03	59224.59	59267.67	57225.13	58368.37	59307.44	52837.85	53867.37	49190.89	49696.90
4.40	44504.56	47353.86	49329.72	46316.51	47608.02	48582.15	42994.25	43941.90	38493.95	40352.78
4.60	36798.61	39775.17	42348.32	38874.17	40368.12	41344.36	36792.19	37546.63	31363.07	34030.24
4.80	31974.78	34955.85	37318.61	33929.15	35624.24	36590.32	31292.76	31881.33	26852.12	29413.22
5.00	28568.23	31264.25	32066.15	30492.48	32352.34	33316.28	26992.27	27419.81	24014.99	26114.99
5.20	25911.68	28561.68	29409.27	27810.87	29779.96	30756.51	24819.20	25044.90	22014.88	23914.89
5.40	24023.31	26627.31	27514.90	25899.98	27954.59	28919.67	23402.71	23436.81	20462.21	22262.21
5.60	22556.14	25109.73	26027.71	24404.57	26520.71	27433.32	22379.83	22232.13	19164.84	20964.84
5.80	21345.76	23840.25	24777.30	23154.37	25309.46	26128.26	21574.21	21255.55	18128.11	19928.11
6.00	20219.14	22738.50	23683.78	22069.50	24243.44	24960.81	20901.17	20424.77	17355.47	19055.47
6.20	19379.69	21691.62	22653.20	21054.95	23222.24	23883.49	20273.65	19655.60	16748.83	18398.83
6.40	18640.36	20854.42	21811.17	20234.95	22394.63	22999.80	19789.83	19048.67	16208.79	17808.78
6.60	18000.11	20104.42	21052.62	19504.57	21652.54	22223.47	19358.37	18514.14	15734.69	17334.69
6.80	17454.96	19438.46	20377.10	18862.41	20999.92	21549.35	18979.97	18053.08	15421.17	16924.83
7.00	16999.08	18851.20	19782.15	18304.75	20436.40	20969.65	18653.93	17664.13	15177.13	16621.54
7.20	16625.53	18335.96	19264.07	17826.29	19958.02	20475.90	18378.27	17344.01	14991.04	16336.35
7.40	16326.80	17885.48	18818.45	17420.74	19558.31	20059.66	18150.10	17088.07	14858.84	16125.28
7.60	16095.13	17492.71	18440.49	17081.40	19229.15	19712.73	17946.00	16890.75	14776.09	15963.92
7.80	15922.65	17151.58	18124.99	16801.40	18961.19	19427.27	17805.58	16733.86	14738.18	15869.69
8.00	15801.34	16857.55	17866.36	16574.02	18743.66	19196.06	17699.50	16638.62	14740.48	15821.98
8.20	15722.74	16608.11	17658.68	16392.77	18563.69	19013.02	17623.38	16582.26	14778.45	15817.22
8.40	15677.17	16403.46	17495.89	16251.48	18405.29	18873.89	17572.96	16557.90	14847.70	15844.06
8.60	15652.20	16247.72	17372.00	16144.28	18249.98	18776.55	17544.33	16558.05	14944.08	15908.31
8.80	15631.56	16149.73	17281.39	16065.53	18082.04	18719.27	17533.97	16573.82	15063.72	15976.09
9.00	15600.50	16122.41	17218.88	16026.60	17896.36	18698.33	17538.86	16593.90	15202.97	16073.77
9.20	15558.18	16145.11	17179.87	15971.51	17700.27	18707.98	17556.46	16605.06	15358.52	16208.00
9.40	15527.26	16215.81	17160.45	15945.33	17507.59	18742.07	17584.66	16598.52	15527.26	16345.71
9.60	15481.41	16313.98	17157.38	15926.08	17332.62	18795.08	17621.71	16577.57	15706.36	16484.05
9.80	15460.61	16428.94	17168.31	15910.40	17187.64	18862.45	17666.13	16552.63	15893.22	16640.41
10.00	15454.05	16552.84	17191.97	15900.24	17081.80	18940.39	17716.63	16531.35	16085.45	16792.42
10.50	15494.02	16854.11	17313.24	15994.26	17005.34	19162.73	17862.18	16523.49	16543.02	17190.02
11.00	15591.93	17055.77	17555.58	16311.94	17142.97	19398.70	18023.15	16600.93	17025.52	17595.52
11.50	15715.68	17158.37	17878.17	16672.08	17411.99	19626.54	18186.61	16741.53	17475.64	17945.62
12.00	15836.73	17212.87	18203.04	16995.29	17756.33	19832.75	18342.60	16930.60	17895.46	18239.57
12.50	15935.97	17243.96	18497.43	17275.98	18125.63	20010.36	18484.57	17149.19	18294.64	18480.36
13.00	16006.84	17262.53	18750.18	17523.90	18480.35	20157.08	18614.23	17382.88	18551.51	18669.19
13.50	16053.99	17277.19	18957.50	17745.33	18802.93	20272.09	18735.90	17621.46	18754.36	18815.50
14.00	16088.54	17296.90	19119.33	17942.99	19064.63	20353.30	18842.68	17856.75	18899.72	18919.28
14.50	16123.02	17330.79	19239.50	18118.33	19280.46	20402.39	18930.52	18081.21	19008.44	19007.24
15.00	16168.51	17386.69	19325.31	18272.78	19447.94	20431.83	18998.74	18287.98	19088.00	19088.00
15.50	16233.45	17469.82	19385.25	18408.02	19574.06	20455.81	19054.51	18471.73	19146.61	19146.61
16.00	16323.32	17582.27	19426.77	18526.06	19667.14	20482.13	19097.78	18629.56	19190.23	19190.23
16.50	16440.54	17723.20	19455.52	18628.98	19735.27	20513.27	19134.11	18761.13	19223.10	19223.10
17.00	16584.56	17889.54	19475.49	18723.78	19785.45	20548.80	19164.79	18878.21	19243.18	19245.88
17.50	16752.42	18076.94	19489.44	18807.24	19823.24	20587.13	19192.56	18980.86	19262.56	19266.06
18.00	16939.64	18280.44	19499.35	18880.83	19852.78	20626.47	19212.72	19068.60	19282.72	19282.72
18.50	17141.06	18495.16	19506.66	18950.75	19877.00	20665.34	19231.71	19124.84	19294.71	19294.71
19.00	17351.57	18716.54	19512.55	19007.97	19897.83	20702.64	19249.29	19166.58	19304.28	19304.28
19.50	17566.44	18940.55	19518.06	19058.31	19916.52	20737.66	19262.01	19203.33	19312.01	19312.01
20.00	17781.45	19173.29	19524.26	19097.48	19933.80	20770.02	19273.29	19230.08	19318.29	19318.29
20.50	17992.80	19381.82	19532.98	19131.13	19950.07	20799.57	19283.44	19250.41	19323.44	19323.44
21.00	18196.91	19534.94	19603.07	19164.88	19965.52	20826.28	19292.70	19268.55	19327.70	19327.70
21.50	18390.22	19553.34	19803.09	19191.64	19980.20	20850.28	19301.23	19281.92	19331.23	19331.23
22.00	18568.89	19574.05	19995.41	19213.56	19994.10	20871.71	19307.19	19292.76	19334.19	19334.19
24.00	19060.63	19748.47	20602.10	19277.63	20041.18	20928.23	19325.10	19322.09	19342.10	19341.50
26.00	19276.56	19965.06	20884.65	19316.56	20074.20	20962.68	19336.34	19335.06	19346.04	19345.84
28.00	19321.25	20063.45	20973.27	19332.25	20095.40	20985.37	19343.75	19342.27	19348.75	19348.75
30.00	19338.21	20099.07	21003.61	19341.21	20108.41	21003.61	19347.21	19346.71	19350.66	19350.56
32.00	19345.84	20113.53	21016.38	19345.84	20116.32	21016.38	19349.27	19349.34	19351.84	19351.84

Table 2. Continuation.

$R(a_0)$	$4^1\Sigma^+$	$5^1\Sigma^+$	$6^1\Sigma^+$	$4^3\Sigma^+$	$5^3\Sigma^+$	$6^3\Sigma^+$	$3^1\Pi$	$3^3\Pi$	$1^1\Delta$	$1^3\Delta$
34.00	19349.05	20120.35	21022.69	19349.05	20121.19	21022.69	19350.75	19350.75	19352.70	19352.70
36.00	19350.78	20124.03	21026.21	19350.78	20124.28	21026.21	19351.93	19351.93	19353.21	19353.21
38.00	19352.18	20126.23	21028.36	19352.21	20126.31	21028.36	19352.77	19352.77	19353.59	19353.59
40.00	19353.05	20127.66	21029.74	19353.05	20127.69	21029.74	19353.44	19353.44	19353.85	19353.85
42.00	19353.50	20128.65	21030.68	19353.50	20128.66	21030.68	19353.96	19353.96	19354.06	19354.06
44.00	19353.81	20129.36	21031.33	19353.81	20129.36	21031.33	19354.31	19354.31	19354.23	19354.23
46.00	19354.04	20129.88	21031.79	19354.04	20129.88	21031.79	19354.53	19354.53	19354.37	19354.37
48.00	19354.21	20130.27	21032.13	19354.21	20130.27	21032.13	19354.67	19354.67	19354.47	19354.47
50.00	19354.35	20130.57	21032.38	19354.35	20130.57	21032.38	19354.67	19354.67	19354.54	19354.54
52.00	19354.45	20130.81	21032.56	19354.45	20130.81	21032.58	19354.68	19354.68	19354.59	19354.59
54.00	19354.55	20131.00	21032.70	19354.54	20131.00	21032.76	19354.68	19354.68	19354.63	19354.63
56.00	19354.63	20131.16	21032.81	19354.63	20131.16	21032.93	19354.69	19354.69	19354.66	19354.66
58.00	19354.69	20131.29	21032.91	19354.69	20131.29	21033.05	19354.69	19354.69	19354.68	19354.68
60.00	19354.70	20131.40	21033.02	19354.70	20131.40	21033.15	19354.70	19354.70	19354.70	19354.70
62.50	19354.70	20131.51	21033.13	19354.70	20131.51	21033.27	19354.70	19354.70	19354.71	19354.71
64.00	19354.71	20131.56	21033.24	19354.71	20131.56	21033.33	19354.71	19354.71	19354.71	19354.71
66.00	19354.71	20131.61	21033.34	19354.71	20131.61	21033.40	19354.71	19354.71	19354.72	19354.72
68.00	19354.72	20131.66	21033.45	19354.72	20131.66	21033.45	19354.72	19354.72	19354.72	19354.72
70.00	19354.73	20131.70	21033.56	19354.73	20131.70	21033.50	19354.73	19354.73	19354.73	19354.73
80.00	19354.73	20131.79	21033.67	19354.73	20131.79	21033.69	19354.73	19354.73	19354.73	19354.73
90.00	19354.74	20131.82	21033.77	19354.74	20131.82	21033.79	19354.74	19354.74	19354.74	19354.74
110.00	19354.74	20131.87	21033.88	19354.74	20131.87	21033.88	19354.74	19354.74	19354.74	19354.74
150.00	19354.75	20131.88	21033.88	19354.75	20131.88	21033.88	19354.75	19354.75	19354.75	19354.75

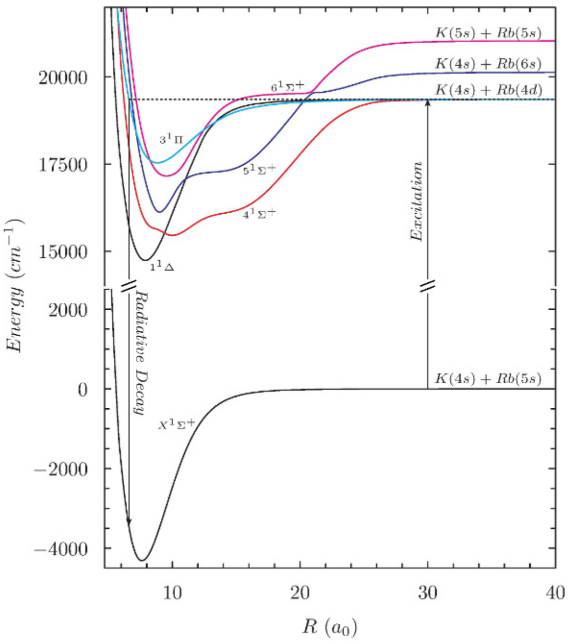

Figure 3. Calculated potential energy curves of the ground and highly excited singlet states. The vertical arrows indicate photoassociation and radiative decay, while the horizontal dotted line corresponds to the K(4s) + Rb(4d) atomic asymptote.

4. Conclusion

We have calculated the adiabatic potential energy curves for excited states of the KRb molecule using CASSCF/MRCI method. Comparisons with available theoretical results and rather scarce experimental data give a valuable estimation of the reliability of the theoretical approach. Our nonrelativistic approach uses the large atomic pseudopotentials and carefully chosen extensive basis of atomic functions. Effectively, we perform only two-electron calculations. This method gives overall reliable results for excited states, which are in good agreement with other recent theoretical results. Overall spectroscopic constants derived from our potential curves also display good agreement with the experimental data of Lee *et al.* [11, 32]. The obtained potential curves and molecular wave functions will help describe photodissociation and photoassociation processes, laying the foundations for future work.

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Table 3. Molecular constants R_e (Å), T_e, D_e, ω_e (cm^{-1}) for the highly excited states of the KRb molecule.

State	Dissociation	Method	R_e	D_e	T_e	ω_e
$4^1\Sigma^+$	$(K(4s) + Rb(4d))$	present work[a]	5.295	3901	19767	39.02
		Rousseau theory [14]	5.265	3816[b]	19648	38.6
		Park theory [15]	5.30	3871	19611	38
		Yiannopoulou theory [13]	6.58		18967	78[c]
$5^1\Sigma^+$	$(K(4s) + Rb(6s))$	present work	4.765	4009	20436	75.95
		Lee exp. [11]			20394.6(37)	75.6(14)
		Rousseau theory [14]	4.761	3818	20393	75.7
		Park theory [15]	4.80	3871	20339	75
$6^1\Sigma^+$	$(K(5s) + Rb(5s))$	present work	5.050	3877	21470	40.69
		Rousseau theory [14]	5.071	3764	21347	40.1
		Park theory [15]	5.10	3790	21315	41
$4^3\Sigma^+$	$(K(4s) + Rb(4d))$	present work	5.300	3455	20213	46.08
		Rousseau theory [14]	5.275	3407	20060	43.7
		Park theory [15]	5.30	3468	19981	59
		Yiannopoulou theory [13]	5.37		19741	39
$5^3\Sigma^+$	$(K(4s) + Rb(6s))$	present work	5.505	3130	21314	64.51
		Rousseau theory [14]	5.497	3030	21175	63
		Park theory [15]	5.48	3146	21106	63
		Yiannopoulou theory [13]	6.58		18967	78
$6^3\Sigma^+$	$(K(5s) + Rb(5s))$	present work	4.780	2336	23011	57.48
		Rousseau theory [14]	4.787	2182	22936	55.5
		Park theory [15]	4.81	2258	22895	56
$3^1\Pi$	$(K(4s) + Rb(4d))$	present work	4.675	1821	21847	40.79
		Rousseau theory [14]	4.758	1562	21883	38.4
		Park theory [15]	4.81	1452	21955	36
		Yiannopoulou theory [13]	5.27		21713	37
$3^3\Pi$	$(K(4s) + Rb(4d))$	present work	5.455	2838	20830	38.12
		Rousseau theory [14]	5.413	2735	20729	40.5
		Park theory [15]	5.45	2742	20732	38
		Yiannopoulou theory [13]	6.06		20277	39
$1^1\Delta$	$(K(4s) + Rb(4d))$	present work	4.175	4620	19047	65.57
		Lee exp. [32]	4.205		18991.01	64.62
		Rousseau theory [14]	4.207	4432	19033	65.4
		Park theory [15]	4.25	4275	19187	65
		Yiannopoulou theory [13]	4.49		18620	60
$1^3\Delta$	$(K(4s) + Rb(4d))$	present work	4.295	3540	20128	63.03
		Lee exp. [11]			19861.535(24)	63.296(34)
		Rousseau theory [14]	4.316	3515	19950	64.0
		Park theory [15]	4.37	3307	20124	64
		Yiannopoulou theory [13]	4.82		19948	60

[a] Spectroscopic constants calculated for isotopes ^{39}K and ^{85}Rb.

[b] All values of D_e referring to [14] were calculated from the T_e constants and asymptotic energies given in [14].

[c] Here, we suspect a misprint in [13], probably it should reads 38.

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