Potential energy curves, transition dipole moments, and radiative lifetimes of KBe molecule*

Ming-Jie Wan(万明杰)[1,†], Cheng-Guo Jin(金成国)[1], You Yu(虞游)[2], Duo-Hui Huang(黄多辉)[1,3], and Ju-Xiang Shao(邵菊香)[1,3]

[1] *Computational Physics Key Laboratory of Sichuan Province, Yibin University, Yibin* 644007, *China*
[2] *College of Optoelectronic Technology, Chengdu University of Information Technology, Chengdu* 610225, *China*
[3] *School of Physics and Electronic Engineering, Yibin University, Yibin* 644007, *China*

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An *ab initio* calculations on the ground and low-lying excited states ($X^2\Sigma^+$, $2^2\Sigma^+$, $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$) of KBe molecule have been performed using multireference configuration interaction (MRCI) plus Davidson corrections (MRCI+Q) approach with all electron basis set aug-cc-pCV5Z-DK for Be and def2-AQZVPP-JKFI for K. The $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$ states are investigated for the first time. Inner shell electron correlations are computed on the potential energy curves (PECs) calculations. The spectroscopic and molecular parameters are also predicted. In addition, The transition properties including transition dipole moment, Franck–Condon factors $q_{v'v''}$, Einstein coefficients $A_{v'v''}$, and the radiative lifetimes $\tau_{v'}$ for the $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ transitions are predicted at the same time.

Keywords: potential energy curves, transition dipole moment, Franck–Condon factors, Einstein coefficients

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1. Introduction

In the last twenty years, a number of interesting concepts have been discussed in cold and ultracold molecules formed from alkali-metal atoms (Alk) of group I and alkaline-earth-metal atoms (AEM) of group II. Photoassociation (PA)[1] is one of the most common approaches to obtain ultracold molecules from ultracold atoms. PA spectroscopy of KRb,[2] Yb_2,[3,4] YbRb,[5] and RbCs[6,7] has been observed.

Spectroscopic parameters, rovibrational levels, transition dipole moments, and Franck–Condon factors are also important data in the study of interactions between ultracold molecules.[8,9] Recently, several theoretical investigations have focused on the electronic structures of ultracold molecules,[8–22] such as MgAlk molecules,[9] SrAlk molecules,[10] AEMLi molecules,[11] KRb,[12] LiBe,[13,14] NaBe,[13,15] KLi,[16] KBe,[17,18] RbBe,[19] CsBe,[19] RbYb,[20] LiYb,[21,22] and our previous works for MgCl,[23] MgBr,[23] BeCl,[24] BeBr,[24] BeI,[25] MgI.[25] There are a few theoretical investigations on the potential energy curves (PECs) of KBe molecule. Bruna *et al.*[17] have given the equilibrium distance and dipole moment for the ground state of KBe molecule for the first time. The PECs of four doublet states with different inner electron correlations were investigated by Xiao *et al.*[18] Four sets of the frozen core orbitals (FCOs) for each electronic state were considered in their work. At first, they kept the 1s orbital of Be and 1s2s2p3s3p orbitals of K as frozen core orbital; then, 1s orbital of Be, 1s2s2p3s orbitals of K; 1s orbital of Be, 1s2s2p orbitals of K, and 1s2s2p orbitals of K were considered FCO. They believed that the spectroscopic parameters based on the last one were more reliable.

In this work, we have carried out the multi-reference configuration interaction (MRCI)[26,27] computations on three $^2\Sigma^+$, two $^4\Pi$, and three $^4\Sigma^+$ states of KBe molecule based on inner shell electron correlations. At the present time, Li,[28] Zhu,[29] Wang,[30] Liu,[31] and Xing[32] have adopted the MRCI method to calculate the ground and low-lying states of CS^+, AsO^+, P_2, GeO, and CF^+, and the obtained results conform to the experimental values. No experimental data have yet been found in the literature for these states, and our main goal is to provide accurate spectroscopic parameters for these states. In addition, the dipole moments, the transition dipole moments (TDMs), Einstein coefficients ($A_{v'v''}$), and Franck–Condon factors ($q_{v'v''}$) are also presented.

2. Computational details

The electronic structure calculations are performed with the MOLPRO 2010 program package.[33] Working in C_{2v} point group symmetry, which has four irreducible representations (A_1, B_1, B_2, and A_2). The A_1 irreducible representation yields Σ^+ states and a component of Δ states; B_1 gives the Π states, and A_2 yields Σ^- states and the other component of Δ

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†Corresponding author. E-mail: wanmingjie1983@sina.com

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states.

Complete active space self-consistent-field (CASSCF) calculations are carried out. Using the CASSCF[34,35] wave functions as a zero-order function, the energies of the Λ–S states are computed via the MRCI method plus Davidson corrections (MRCI+Q).[36,37] Eight electronic states ($X^2\Sigma^+$, $2^2\Sigma^+$, $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, $3^4\Sigma^+$) are investigated in the present work. The PECs for the $^2\Sigma^+$, $^4\Sigma^+$, and $^4\Pi$ states are calculated separately. To improve the quality of PECs, core–valence correlations are computed in PECs calculations in MRCI+Q step. In CASSCF step, the 1s2s2p orbitals of K are doubly closed, which are frozen orbitals, 1s of Be and 3s3p of K are closed-shell orbitals, the 2s2p orbitals of Be and 4s4p3d orbitals of K are the active orbitals. Considering electron correlation effect in the MRCI+Q step, the 1s2s2p orbitals of K are core orbitals, 1s of Be and 3s3p of K are closed-shell orbitals, therefore, 13 electrons are correlation electrons.

In the present work, the all electron basis set aug-cc-pCV5Z-DK for Be[38] and def2-AQZVPP-JKFI for K[39] are chosen in all calculations. The spectroscopic and molecular parameters are determined with Le Roy's LEVEL 8.0 program.[40] The PECs calculations are performed with an interval of 0.1 Å over the distance from 2.3 Å to 30 Å for three $^2\Sigma^+$ and two $^4\Pi$ states and 3.5 Å to 30 Å for three $^4\Sigma^+$ states, and the value decreases to 0.02 Å near R_e.

3. Results and discussion

3.1. PECs

The PECs for three $^2\Sigma^+$, two $^4\Pi$, and three $^4\Sigma^+$ electronic states of KBe molecule are performed, which are illustrated in Figs. 1–3, respectively. We can see that the PECs for all states are smooth. For convenient of discussion, the eight bound electronic states are divided into two categories in the discussion, i.e., the PECs for the doublet ($^2\Sigma^+$) and quartet ($^4\Pi$, $^4\Sigma^+$) electronic states, respectively.

3.2. PECs for the $^2\Sigma^+$ states

The dominant electronic configurations at R_e for these eight states are tabulated in Table 1. We can see that the dominant compositions for the ground state $X^2\Sigma^+$ at R_e is $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma 2\pi^4$; the dominant compositions for the $2^2\Sigma^+$ state can be represented by three main configurations, $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma 2\pi^4$, $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 9\sigma 2\pi^4$, and $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 10\sigma 2\pi^4$; the $3^2\Sigma^+$ state can be represented by $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 9\sigma 2\pi^4$ and $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 10\sigma 2\pi^4$. The electronic transition $2^2\Sigma^+ \rightarrow X^2\Sigma^+$ and $3^2\Sigma^+ \rightarrow X^2\Sigma^+$ both arise from $8\sigma \rightarrow 9\sigma$ and $8\sigma \rightarrow 10\sigma$ electron promotions.

Table 1. Important electronic configurations of KBe at the equilibrium separations.

States	Dominant electronic configurations at R_e
$X^2\Sigma^+$	$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma 2\pi^4$ (63.42%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 10\sigma 2\pi^4$ (11.04%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 9\sigma 2\pi^4$ (9.25%) $4\sigma^2 5\sigma^2 6\sigma^2 8\sigma 2\pi^4 3\pi^2$ (3.49%)
$2^2\Sigma^+$	$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma 2\pi^4$ (15.02%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 10\sigma 2\pi^4$ (28.26%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 9\sigma 2\pi^4$ (37.75%) $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma^2 2\pi^4$ (2.92%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 9\sigma 2\pi^4 3\pi^2$ (2.08%)
$3^2\Sigma^+$	$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 10\sigma 2\pi^4$ (45.19%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 9\sigma 2\pi^4$ (38.65%), $4\sigma^2 5\sigma^2 6\sigma^2 10\sigma 2\pi^4 3\pi^2$ (2.67%) $4\sigma^2 5\sigma^2 6\sigma^2 9\sigma 2\pi^4 3\pi^2$ (2.08%)
$1^4\Pi$	$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 2\pi^4 3\pi$ (78.41%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 9\sigma 2\pi^4 3\pi$ (11.21%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 9\sigma 2\pi^4 4\pi$ (1.75%)
$1^4\Sigma^+$	$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 9\sigma 2\pi^4$ (65.59%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 10\sigma 2\pi^4$ (27.34%)
$2^4\Pi$	$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 2\pi^4 3\pi$(5.44%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 9\sigma 2\pi^4 3\pi$ (81.50%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 2\pi^4 4\pi$ (4.73%)
$2^4\Sigma^+$	$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 9\sigma 2\pi^4$ (20.50%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 10\sigma 2\pi^4$ (49.09%), $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 2\pi^4 3\pi 4\pi$ (23.51%)
$3^4\Sigma^+$	$4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 2\pi^4 3\pi 4\pi$ (92.74%)

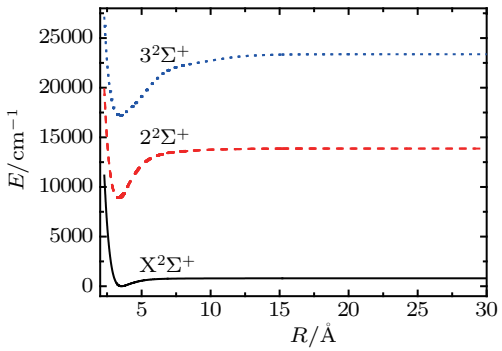


Fig. 1. (color online) PECs for the $X^2\Sigma^+$, $2^2\Sigma^+$, and $3^2\Sigma^+$ states of KBe.

The PECs for the $X^2\Sigma^+$, $2^2\Sigma^+$, and $3^2\Sigma^+$ states of KBe are plotted in Fig. 1. To our best knowledge, there are not experimental data on spectroscopic parameters of KBe. In previous theoretical studies, Xiao *et al.*[18] have investigated PECs for the $X^2\Sigma^+$ and $2^2\Sigma^+$ states at the same level, they also given the results of spectroscopic parameters. Compared the results for the $X^2\Sigma^+$ and $2^2\Sigma^+$ states between ours and Xiao's,[18] the percentage errors are: for the $X^2\Sigma^+$ state, $\delta R_e/R_e = 1.99\%$ (Ref. [18]), $\delta\omega_e/\omega_e = 3.55\%$ (Ref. [18]), $\delta D_e/D_e = 19.16\%$ (Ref. [18]), for $2^2\Sigma^+$ state, $\delta R_e/R_e = 0.07\%$ (Ref. [18]), $\delta\omega_e/\omega_e = 14.49\%$ (Ref. [18]), $\delta D_e/D_e = 4.29\%$ (Ref. [18]). There are large errors of D_e and ω_e between ours and Xiao's results, and the reason may be that the $3^2\Sigma^+$ state is considered in the CASSCF and MRCI+Q steps. We also calculate only two $^2\Sigma^+$ states at the same level. R_e in-

creased and D_e decreased for the ground state when the third 3sigma is considered. $\Delta R_e = 0.0302$ Å ($\Delta R_e/R_e = 0.86\%$), $\Delta\omega_e = 7.5$ cm^{-1} ($\Delta\omega_e/\omega_e = 6.31\%$), $\Delta\omega_e\chi_e = 0.2346$ cm^{-1} ($\Delta\omega_e\chi_e/\omega_e\chi_e = 5.48\%$), and $\Delta D_e = 83.4$ cm^{-1} ($\Delta D_e/D_e = 9.46\%$). The $3^2\Sigma^+$ state may play a very important role, and influence the spectroscopic properties for the $X^2\Sigma^+$ and $2^2\Sigma^+$.

Augustovičvá *et al.*[9] and Guérout *et al.*[10] have investigated the ground state for AEM–Alk (AEM = Mg and Sr; Alk = Li, Na, K, Rb, and Cs) at RCCSD(T) and FCI level, respectively, for both MgAlk and SrAlk molecules. R_e increases and D_e decreases with the increase of the atomic weight of Alk, i.e., R_e are 3.100, 3.529, 4.087, 4.286, and 4.518 Å; D_e are 1414.6, 808.4, 637.5, 578.5, and 558.2 cm^{-1} for LiMg, NaMg, KMg, RbMg, and CsMg,[9] respectively. R_e is 3.476, 3.819, and 4.407 Å; D_e is 2587, 1597, and 1166 cm^{-1} for LiSr, NaSr, and KSr,[10] respectively. Be, Mg, and Sr in periodic table belongs to group II, the properties of AEM–Alk are similar. R_e and D_e for the ground state of LiBe, NaBe, RbBe, and CsBe molecules are 2.607,[13] 3.052,[13] 3.762,[19] 4.049 Å,[19] and 2340,[13] 1129.2,[13] 761.2,[19] and 418.6 cm^{-1}[19] by Bauschlicher *et al.* and Yang *et al.*, respectively. The results for the ground state of KBe molecule are as follows: $R_e = 3.5421$ Å and $D_e = 798.48$ cm^{-1}, respectively. Same to MgAlk and SrAlk molecules, R_e(CsBe) > R_e(RbBe) > R_e(KBe) > R_e(NaBe) > R_e(LiBe), and D_e(CsBe) < D_e(RbBe) < D_e(KBe) < D_e(NaBe) < D_e(LiBe).

The PECs for the $3^2\Sigma^+$ electronic state are studied for the first time. We have given the spectroscopic parameters based on inner electrons correlation. All spectroscopic parameters for the three $^2\Sigma^+$ states are listed in Table 2. Thought there are not experimental data of spectroscopic parameters, we have provided other reference values of spectroscopic parameters for the first three $^2\Sigma^+$ states.

Table 2. Spectroscopic parameters for eight low–lying states of KBe.

States		T_e/cm^{-1}	R_e/Å	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	D_e/cm^{-1}	B_e/cm^{-1}
$X^2\Sigma^+$	This work[a]	0	3.5421	111.36	4.0475	798.48	0.1836
	Cal.[b]		3.5243				
	Cal.[c]		3.585	107.538	6.827	670.52	0.182
$2^2\Sigma^+$	This work[a]	8897.19	3.3086	200.49	1.7069	4975.46	0.2103
	Cal.[c]		3.311	175.981	–2.637	4779.63	0.204
$3^2\Sigma^+$	This work[a]	17213.98	3.3963	144.32	1.4823	6157.58	0.1995
$1^4\Pi$	This work[a]	19335.14	3.2237	201.23	2.2722	3485.74	0.2215
$1^4\Sigma^+$	This work[a]	22783.06	6.3397	14.129	2.1832	24.927	0.0588
$2^4\Pi$	This work[a]	28694.39	3.6342	124.12	–0.0707	7205.68	0.1743
$2^4\Sigma^+$	This work[a]	35796.99	8.5900	11.619	0.3020	98.330	0.0312
$3^4\Sigma^+$	This work[a]	35910.78	7.3300	9.3496	0.8660	22.178	0.0431

[a]The results are obtained by using MRCI+Q method with CV + DK corrections.
[b]Ref. [17].
[c]Ref. [18].

3.3. The PECs for quartet states

The dominant electronic configurations at R_e for the $1^4\Pi$ and $2^4\Pi$ are $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 2\pi^4 3\pi$ and $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 9\sigma 2\pi^4 3\pi$, which is $8\sigma \rightarrow 9\sigma$ electron promotion for the $2^4\Pi \rightarrow 1^4\Pi$ electronic transition. The $1^4\Pi$ is the ground quartet state, which corresponds to the dissociation channel Be(^{3}P) + K(^{2}P), and has the lowest energy at R_e, because the lower dissociation channel Be(^{1}S) + K(^{2}P) can only obtain one doublet Π state.

The dominant electronic configurations at R_e for the $1^4\Sigma^+$ are $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 9\sigma 2\pi^4$ and $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 10\sigma 2\pi^4$; the dominant electronic configurations at R_e for the $2^4\Sigma^+$ are $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 9\sigma 2\pi^4$, $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 8\sigma 10\sigma 2\pi^4$, and $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 2\pi^4 3\pi 4\pi$; and the dominant electronic configurations at R_e for the $3^4\Sigma^+$ is $4\sigma^2 5\sigma^2 6\sigma^2 7\sigma 2\pi^4 3\pi 4\pi$. Therefore, the electronic transition from a state to another at R_e can be obtained.

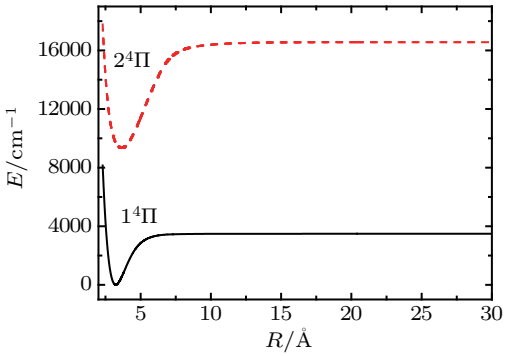


Fig. 2. (color online) PECs for the $1^4\Pi$ and $2^4\Pi$ states of KBe.

The PECs and spectroscopic parameters for quartet states have been investigated for the first time, the $1^4\Pi$ and $2^4\Pi$ states in Fig. 2 and the $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$ states in Fig. 3. From Fig. 3, it can be seen that the avoided crossing of $2^4\Sigma^+$ and $3^4\Sigma^+$ states occurred at about 6.0 Å. The energy difference $\Delta E = E(3^4\Sigma^+) - E(2^4\Sigma^+)$ between these two $^4\Sigma^+$ states is only

1.909 cm^{-1} at $R = 6$ Å. All spectroscopic parameters for two $^4\Pi$ and three $^4\Sigma^+$ states are listed in Table 2. D_e for the $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$ states are 24.927, 98.330, and 22.178 cm^{-1}, respectively. They are shallow potential wells.

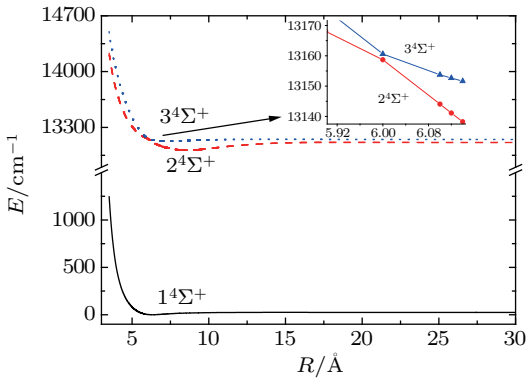


Fig. 3. (color online) PECs for the $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$ states of KBe.

Table 3. The vibrational levels G_υ ($J = 0$) and inertial rotation constants B_υ for the ground state $X^2\Sigma^+$ of KBe.

	Gυ		B_υ
υ	This work	Cal.[a]	This work
0	55.5631	50.2521	0.18005
1	160.1901	144.2110	0.17299
2	255.9636	227.9657	0.16559
3	342.9322	301.9383	0.15783
4	421.2299	366.8494	0.14975
5	491.0946	423.4874	0.14136
6	552.8157	472.8025	0.13268
7	606.7248	515.4564	0.12368
8	653.1215	552.1002	0.11428
9	692.196	583.2932	0.10423
10	723.9683	609.4008	0.09313
11	748.4093	630.3685	0.08086
12	766.2115	646.2968	0.06867
13	778.8442	658.0773	0.05709
14	787.2764	665.6890	0.04498
15	792.2271	669.5049	0.03359
16	795.3817		0.02736
17	797.7765		0.02132

[a]Ref. [18].

3.4. Molecular parameters

Based on the reliable PECs for the bound states ($X^2\Sigma^+$, $2^2\Sigma^+$, $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$), we have determined their vibrational levels G_υ and inertial rotation constants B_υ when J= 0. G_υ and B_υ for the ground state together with Xiao's results[18] are collected in Table 3, the other data are collected in Supplementary Material. Compared with the results of Xiao *et al.*,[18] we overestimate the G_υ for the ground state. From Supplementary Material, the first 21 levels of G_υ for the $2^2\Sigma^+$ state are close to the results of Xiao *et al.*[18] The largest error is only about 2.6%, which is in agreement with the results of D_e.

The highest vibrational level for the ground state $X^2\Sigma^+$ is $\upsilon = 17$ in our work. This level lies 0.7035 cm^{-1} below the dissociation limit, or the energy of 99.91% for D_e. The level is $\upsilon = 60$ for the $2^2\Sigma^+$ state, which lies 0.013 cm^{-1} below the dissociation limit, the energy of almost 100% for D_e. The highest vibrational level for the ground state $X^2\Sigma^+$ obtained by Xiao *et al.*[18] is $\upsilon = 15$, which lies 1.02 cm^{-1} below the dissociation limit, the energy of 99.85% for D_e.

Inertial rotation constants B_υ for states ($X^2\Sigma^+$, $2^2\Sigma^+$, $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$) are also listed in Supplementary Material. Based on the accuracy of calculations, we believe that the values of G_υ and B_υ for these eight states are reliable.

3.5. Dipole moments, transition dipole moments, and radiative lifetimes

The dipole moment as a function of R is plotted in Fig. 4, for the $X^2\Sigma^+$, $2^2\Sigma^+$, $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$ states. It is clearly seen that the avoided crossing position between the $2^4\Sigma^+$ and $3^4\Sigma^+$ states occurs at about 6.0 Å. The dipole moments for eight states approach zero at large interatomic distance. We can say that the dissociation channels for these eight states are the sum of neutral K atom and Be atom. Dipole moments at R_e for eight states are listed in Table 4.

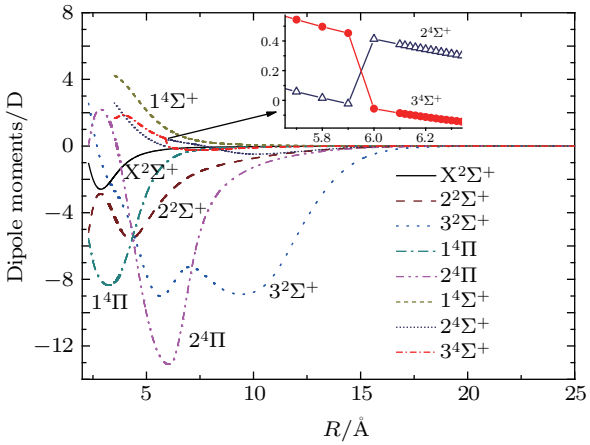


Fig. 4. (color online) Dipole moments for the $X^2\Sigma^+$, $2^2\Sigma^+$, $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$ states of KBe.

Table 4. Dipole moments at the equilibrium distance for the eight states of KBe.

Ref.	$X^2\Sigma^+$	$2^2\Sigma^+$	$3^2\Sigma^+$	$1^4\Pi$	$1^4\Sigma^+$	$2^4\Pi$	$2^4\Sigma^+$	$3^4\Sigma^+$
This work	–1.748	–3.748	–2.494	–8.361	0.745	–0.241	–0.263	–0.233
Cal.[a]	–1.683							
Cal.[b]	–1.549	–6.033						

[a]Ref. [17].
[b]Ref. [18].

Notable, for one-electron and two-electron systems, the dipole moments for the ground state at R_e for KBe and LiYb[22] are 1.748 and 0.03 Debye (D), respectively; and the electronegativities (EN) of Li, K, Be, and Yb atoms are 0.98, 0.82, 1.57, and 1.06 eV, respectively. It is clearly seen that the difference of EN between K and Be is 0.75 eV, but the value is only 0.08 eV between Li and Yb. Therefore, KBe

has a sizable dipole moment, but LiYb does not. For Alk-Be series, the dipole moments are 2.415,[14] 1.978,[15] 1.748, 1.302,[19] and 1.046 D[19] for the ground state of LiBe, NaBe, KBe, RbBe, and CsBe molecules, respectively. It can be seen that the dipole moments for the ground state decrease with the increase of the atomic weight of Alk.

Figure 5 shows the transition dipole moment functions (TDMs) for the $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ systems of KBe molecule. Notable the transitions for the $2^2\Sigma^+$–$X^2\Sigma^+$ and $2^4\Pi$–$1^4\Sigma^+$ have the same asymptotic limit, and come from an allowed transition $^2S\rightarrow{}^2P$ of K atom at large interatomic distance. Our calculation results at $R = 30$ Å are 7.8185 and 7.8124 D, respectively. Xiao *et al.*[18] obtains the value 8.17 D for the $2^2\Sigma^+$–$X^2\Sigma^+$ bond system, which is about 0.25 D bigger than our results. The $3^2\Sigma^+$–$X^2\Sigma^+$ system is $^1S\rightarrow{}^3P$ transition of Be atom at large interatomic distance, which is a forbidden transition. The TDMs for the $3^2\Sigma^+$–$X^2\Sigma^+$ system decreases and tends to be zero at large interatomic distance.

Transition probabilities for emission including Einstein coefficients $A_{\upsilon'\upsilon''}$ and Franck–Condon factors $q_{\upsilon'\upsilon''}$ for the $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$2^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ band systems have been evaluated, which are tabulated in Table 5. The values for transitions from the vibrational levels of a higher state to the vibrational levels of a lower state are listed in Table 5. For the first five vibrational levels ($\upsilon' = 0$, 1, 2, 3, 4) for the $2^2\Sigma^+$–$X^2\Sigma^+$ system, the stronger transitions occur from $\upsilon' = 0$ to $\upsilon'' = 0$, 1, 2, 3; $\upsilon' = 1$ to $\upsilon'' = 0$, 2, 3, 4, 5, 6; $\upsilon' = 2$ to $\upsilon'' = 0$, 1, 2, 6, 7, 8; $\upsilon' = 3$ to $\upsilon'' = 0$, 1, 4; and $\upsilon' = 4$ to $\upsilon'' = 1$, 3. We can clearly see that both $A_{\upsilon'\upsilon''}$ and $q_{\upsilon'\upsilon''}$ are concordant on this prediction for the calculated transition systems.

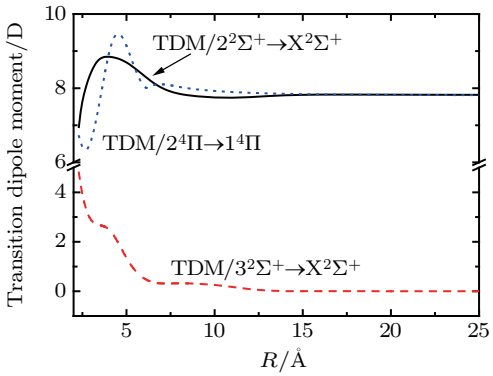


Fig. 5. (color online) Transition dipole moments for the $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ transitions of KBe.

Table 5. Einstein spontaneous emission coefficients $A_{\upsilon'\upsilon''}$ (in s^{-1}) and Franck–Condon factors $q_{\upsilon'\upsilon''}$ (in italics) for the $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$2^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ band systems of KBe.

υ'/υ''	$2^2\Sigma^+$–$X^2\Sigma^+$[a]									
	0	1	2	3	4	5	6	7	8	9
0	5.889(6)	5.365(6)	2.932(6)	1.292(6)	5.143(5)	1.974(5)	7.601(4)	2.999(4)	1.229(4)	5.266(3)
	3.343(–1)	3.262(–1)	1.860(–1)	8.540(–2)	3.541(–2)	1.415(–2)	5.667(–3)	2.325(–3)	9.892(–4)	4.398(–4)
1	6.070(6)	1.511(5)	1.216(6)	2.639(6)	2.474(6)	1.708(6)	1.028(6)	5.810(5)	3.211(5)	1.771(5)
	3.261(–1)	8.171(–3)	7.171(–2)	1.604(–1)	1.553(–1)	1.106(–1)	6.858(–2)	3.987(–2)	2.260(–2)	1.276(–2)
2	3.819(6)	1.447(6)	2.522(6)	3.996(5)	1.219(5)	8.821(5)	1.371(6)	1.390(6)	1.158(6)	8.662(5)
	1.916(–1)	7.556(–2)	1.355(–1)	2.178(–2)	7.368(–3)	5.314(–2)	8.429(–2)	8.732(–2)	7.422(–2)	5.651(–2)
3	1.877(6)	3.736(6)	3.880(5)	8.029(5)	1.661(6)	8.742(5)	1.389(5)	1.265(4)	1.899(5)	3.669(5)
	8.846(–2)	1.824(–1)	1.942(–2)	4.187(–2)	8.858(–2)	4.744(–2)	7.499(–3)	8.372(–4)	1.153(–2)	2.236(–2)
4	7.749(5)	3.941(6)	4.130(5)	2.054(6)	3.724(5)	1.274(5)	7.623(5)	9.225(5)	6.537(5)	3.330(5)
	3.441(–2)	1.810(–1)	1.964(–2)	1.001(–1)	1.850(–2)	6.610(–3)	3.999(–2)	4.912(–2)	3.522(–2)	1.807(–2)
υ'/υ''	$3^2\Sigma^+$–$X^2\Sigma^+$									
	0	1	2	3	4	5	6	7	8	9
0	8.010(6)	2.639(6)	6.370(5)	1.507(5)	3.870(4)	1.128(4)	3.777(3)	1.441(3)	6.165(2)	2.902(2)
	6.999(–1)	2.282(–1)	5.465(–2)	1.274(–2)	3.182(–3)	8.890(–4)	2.825(–4)	1.018(–4)	4.117(–5)	1.840(–5)
1	2.857(6)	2.756(6)	3.356(6)	1.582(6)	5.878(5)	2.109(5)	7.942(4)	3.232(4)	1.431(4)	6.853(3)
	2.537(–1)	2.424(–1)	2.895(–1)	1.354(–1)	4.993(–2)	1.769(–2)	6.529(–3)	2.586(–3)	1.109(–3)	5.136(–4)
2	4.567(5)	4.087(6)	1.859(5)	2.193(6)	2.071(6)	1.205(6)	6.031(5)	2.923(5)	1.443(5)	7.395(4)
	4.139(–2)	3.689(–1)	1.701(–2)	1.901(–1)	1.770(–1)	1.023(–1)	5.089(–2)	2.447(–2)	1.195(–2)	6.045(–3)
3	4.598(4)	1.392(6)	3.245(6)	4.190(5)	4.592(5)	1.414(6)	1.421(6)	1.024(6)	6.482(5)	3.909(–2)
	4.581(–3)	1.298(–1)	3.006(–1)	3.636(–2)	4.066(–2)	1.217(–1)	1.209(–1)	8.650(–2)	5.451(–2)	3.273(–2)
4	3.588(3)	2.551(5)	2. 385(6)	1.164(6)	1.586(6)	9.571(4)	2.246(5)	7.169(5)	8.693(5)	7.625(5)
	4.137(–4)	2.619(–2)	2.297(–1)	1.130(–1)	1.436(–1)	8.093(–3)	1.989(–2)	6.174(–2)	7.396(–2)	6.442(–2)
υ'/υ''	$2^4\Pi$ – $1^4\Pi$									
	0	1	2	3	4	5	6	7	8	9
0	9.420(5)	2.672(6)	3.820(6)	3.381(6)	2.063(6)	8.853(5)	2.601(5)	4.932(4)	5.365(3)	2.287(2)
	6.643(–2)	1.888(–1)	2.707(–1)	2.406(–1)	1.474(–1)	6.346(–2)	1.868(–2)	3.534(–3)	3.811(–4)	1.571(–5)
1	2.580(6)	2.735(6)	5.284(5)	2.971(5)	2.121(6)	2.896(6)	1.965(6)	7.651(5)	1.712(5)	1.845(4)
	1.820(–1)	1.932(–1)	3.759(–2)	2.087(–2)	1.505(–1)	2.067(–1)	1.407(–1)	5.482(–2)	1.223(–2)	1.301(–3)
2	3.504(6)	5.865(5)	6.444(5)	1.827(6)	3.650(5)	4.363(5)	2.360(6)	2.642(6)	1.351(6)	3.336(5)
	2.476(–1)	4.150(–2)	4.534(–2)	1.295(–1)	2.618(–2)	3.071(–2)	1.679(–1)	1.887(–1)	9.658(–2)	2.372(–2)
3	3.129(6)	1.201(5)	1.742(6)	1.329(5)	9.426(5)	1.294(6)	4.290(3)	1.416(6)	2.908(6)	1.878(6)
	2.215(–1)	8.458(–3)	1.230(–1)	9.519(–3)	6.653(–2)	9.224(–2)	3.515(–4)	1.003(–1)	2.072(–1)	1.338(–1)
4	2.092(6)	1.337(6)	6.300(5)	6.785(5)	9.983(5)	8.115(4)	1.401(6)	3.379(5)	6.838(5)	2.902(6)
	1.486(–1)	9.452(–2)	4.453(–2)	4.773(–2)	7.084(–2)	5.616(–3)	9.960(–2)	2.448(–2)	4.805(–2)	2.074(–1)

[a]The values in parentheses are the exponents, e.g., 5.889(6) equals 5.889×10^6.

The radiative lifetimes can be calculated as the reciprocal of total Einstein spontaneous emission coefficient,

$$\tau = 1/\sum_{v''} A_{v'v''}.$$

The lifetime of the first 11 vibrational levels for the $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ transitions of KBe are listed in Table 6. We can see that three transitions are strong. When $v' = 0$, the lifetimes are 61.28, 87.01, and 71.03 ns for the $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ transitions, respectively.

Table 6. Radiative lifetime (in ns) of the transitions $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ band systems of KBe molecule.

v'	Radiative lifetime/ns		
	$2^2\Sigma^+$–$X^2\Sigma^+$	$3^2\Sigma^+$–$X^2\Sigma^+$	$2^4\Pi$–$1^4\Pi$
0	61.28	87.01	71.03
1	60.28	87.03	71.03
2	64.09	87.71	71.01
3	85.14	90.79	70.96
4	94.96	103.6	70.87
5	98.97	141.3	70.76
6	102.0	172.4	70.62
7	107.7	190.8	70.46
8	103.0	261.7	70.28
9	109.5	298.2	70.09
10	108.0	380.8	69.89

4. Conclusion and perspectives

In this paper, the potential energy curves (PECs) for electronic states ($X^2\Sigma^+$, $2^2\Sigma^+$, $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$) of KBe molecule are performed by using highly accurate multireference configuration interaction (MRCI) with aug-cc-pCV5Z-DK for Be atom and def2-AQZVPP-JKFI for K atom.

The spectroscopic parameters for these states are also predicted. The $1^4\Pi$ is the ground quartet state, three quartet Σ^+ electronic states are shallow potential wells. Based on the accurate results of PECs, molecular parameters for these eight states are also obtained by solving the radial Schrödinger equation. The dipole moments, transition dipole moments, Franck–Condon factors $q_{v'v''}$, Einstein coefficients $A_{v'v''}$ and the radiative lifetimes $\tau_{v'}$ for the $2^2\Sigma^+$–$X^2\Sigma^+$, $3^2\Sigma^+$–$X^2\Sigma^+$, and $2^4\Pi$–$1^4\Pi$ transitions are also predicted at the same time. The $3^2\Sigma^+$, $1^4\Pi$, $2^4\Pi$, $1^4\Sigma^+$, $2^4\Sigma^+$, and $3^4\Sigma^+$ states are investigated for the first time.

References

[1] Jones K M, Tiesinga E, Lett P D and Julienne P S 2006 *Rev. Mod. Phys.* **78** 483

[2] Wang D, Qi J, Stone M F, Nikolayeva O, Wang H, Hattaway B, Gensemer S D, Gould P L, Eyler E E and Stwalley W C 2004 *Phys. Rev. Lett.* **93** 243005

[3] Takasu Y, Komori K, Honda K, Kumakura M, Yabuzaki T and Takahashi Y 2004 *Phys. Rev. Lett.* **93** 123202

[4] Kitagawa M, Enomoto K, Kasa K, Takahashi Y, Ciurylo R, Naidon P and Julienne P S 2008 *Phys. Rev. A* **77** 012719

[5] Nemitz N, Baumer F, Münchow F, Tassy S and Görlitz A 2009 *Phys. Rev. A* **79** 061403

[6] Kerman A J, Sage J M, Sanis S, Bergeman T and Demille D 2004 *Phys. Rev. Lett.* **92** 033004

[7] Kerman A J, Sage J M, Sanis S, Bergeman T and Demille D 2004 *Phys. Rev. Lett.* **92** 153001

[8] Lane I C 2012 *Phys. Chem. Chem. Phys.* **14** 15078

[9] Augustovičová L and Soldán P 2012 *J. Chem. Phys.* **136** 084311

[10] Guérout R, Aymar M and Dulieu O 2010 *Phys. Rev. A* **82** 042508

[11] Gopakumar G, Abe M, Kajita M and Hada M 2011 *Phys. Rev. A* **84** 062514

[12] Chen K, Yang C L, Wang M S, Ma X G and Liu W W 2012 *Spectrochim. Acta A* **99** 57

[13] Bauschlicher Jr., C.W., Langhoff S R and Partridge H 1992 *J. Chem. Phys.* **96** 1240

[14] Svetlana K, Alexander P, Maria L, Jacek K and Paul S J 2011 *J. Chem. Phys.* **135** 164108

[15] Pablo J B and Friedrich G 2002 *Mol. Phys.* **100** 1681

[16] Xiao K L, Yang C L, Wang M S, Ma X G and Liu W W 2013 *J. Quant. Spectrosc. Radiat. Transf.* **129** 8

[17] Bruna P J and Grein F 2002 *Mol. Phys.* **100** 1681

[18] Xiao K L, Yang C L, Wang M S, Ma X G and Liu W W 2013 *J. Chem. Phys.* **139** 074305

[19] You Y, Yang C L, Wang M S, Ma X G, Liu W W and Wang L Z 2015 *J. Quant. Spectrosc. Radiat. Transf.* **165** 56

[20] Tohme S N and Korek M 2013 *Chem. Phys.* **410** 37

[21] Gopakumar G, Abe M, Das B P, Hada M and Hirao K 2010 *J. Chem. Phys.* **133** 124317

[22] Zhang P, Sadeghpour H R and Dalgarno A 2010 *J. Chem. Phys.* **133** 044306

[23] Wan M J, Shao J X, Gao Y F, Huang D H, Yang J S, Cao Q L, Jin C G and Wang F H 2015 *J. Chem. Phys.* **143** 024302

[24] Wan M J, Shao J X, Huang D H, Jin C G, Yu Y and Wang F H 2015 *Phys. Chem. Chem. Phys.* **17** 26731

[25] Wan M J, Huang D H, Shao J X, Yu Y, Li S and Li Y Y 2015 *J. Chem. Phys.* **143** 164312

[26] Werner H J and Knowles P J 1988 *J. Chem. Phys.* **89** 5803

[27] Knowles P J and Werner H J 1988 *Chem. Phys. Lett.* **145** 514

[28] Li R, Wei C L, Sun Q X, Sun E P, Jin M X, Xu H F and Yan B 2013 *Chin. Phys. B* **22** 123103

[29] Zhu Z L, Qiao H, Lang J H and Sun J F 2013 *Chin. Phys. B* **22** 103102

[30] Wang J M, Feng H Q, Sun J F and Shi D H 2012 *Chin. Phys. B* **21** 023102

[31] Liu X J, Miao F J, Li R, Zha C H, Li Q N and Yan B 2015 *Acta Phys. Sin.* **64** 123101 (in Chinese)

[32] Xing W, Liu H, Shi D H, Sun J F and Zhu Z L 2016 *Acta Phys. Sin.* **65** 033102 (in Chinese)

[33] Werner H J, Knowles P J, Lindh R, *et al.* MOLPRO, version 2010.1 http:www.molpro.net

[34] Knowles P J and Werner H J 1985 *J. Chem. Phys.* **82** 5053

[35] Knowles P J and Werner H J 1985 *Chem. Phys. Lett.* **115** 259

[36] Werner H J and Knowles P J 1988 *J. Chem. Phys.* **89** 5803

[37] Knowles P J and Werner H J 1988 *Chem. Phys. Lett.* **145** 514

[38] Prascher B, Woon D E, Peterson K A, Dunning Jr. T H and Wilson A K 2011 *Theor. Chem. Acc.* **128** 69

[39] Weigend F 2008 *J. Comput. Chem.* **29** 167

[40] Roy R J Le. LEVEL 8.0: *A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels*. Chemical Physics Research Report CP-663 (University of Waterloo, 2007)