

Analytical potential energy function and spectroscopy parameters for B¹Π state of KH

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Multi-reference configuration interaction is used to produce potential energy curves (PECs) for the excited B¹Π state of KH molecule. To investigate the correlation effect of core-valence electrons, five schemes are employed which include the different correlated electrons and different active spaces. The PECs are fitted into analytical potential energy functions (APEFs). The spectroscopic parameters, ro-vibrational levels, and transition frequencies are determined based on the APEFs and compared with available experimental and theoretical data. The molecular properties for B¹Π obtained in this letter, which are better than those available in literature, can be reproduced with calculations using the suitable correlated electrons and active space of orbitals.

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Potassium hydrides have been studied extensively through experimental measurements and theoretical research. Yang *et al.*^[1] showed isotopically combined spectroscopic constants obtained by Rydberg-Klein-Ree (RKR) potential energy curves (PECs) up to $\nu'' = 4$ and $\nu'' = 26$ for the X¹Σ⁺ and A¹Σ⁺ states. Giroud *et al.* calculated the X¹Σ⁺ RKR potential curve for KH to $\nu'' = 14$ ^[2]. Hussein *et al.* extended the RKR potential curve of the X¹Σ⁺ state to $\nu = 23$ ^[3]. Zemke *et al.* constructed a potential energy curve for the ground state of KH and determined that $D_e = 14\,772.7 \pm 0.6$ cm⁻¹^[4]. Jeung *et al.* proposed the perturbative treatment of core-valence correlation effects. Results show that the valence correlation slightly diminishes the core-valence correlation which plays a very important role in the spectroscopy of KH for the ground state^[5]. To test the iterative difference dedicated configuration interaction method, García *et al.* calculated the three lowest Σ⁺ potential curves of KH at the level of CAS-MP2 and obtained the spectroscopic parameters within 0.1 eV which differs with the experimental values^[6]. Lee *et al.* calculated the ¹Σ⁺ and ³Σ⁺ states of KH which were dissociated into the 4s-6p states of K at the level of the configuration interactions and found that most of states show the undulating potential curves^[7]. Khelifi *et al.* performed *ab initio* adiabatic and diabatic studies of the KH molecular for all the states below the ionic limit [i.e., K(4s, 4p, 5s, 3d, 5p, 4d, 6s, and 4f)+H(1s)] in ¹Σ⁺ and ³Σ⁺ symmetries at the level of full valence CI approaches^[8]. They presented the spectroscopic constants for the states and obtained seven vibrational levels of B¹Π.

In contrast to the intense interest in Σ⁺ states, relatively minimal attention has been accorded on B¹Π state. Recently, Lee *et al.* observed the B¹Π excited state for the first time^[9] and obtained several ro-vibrational levels and spectroscopic constants which could be used as a reference standard for theoretical calculation. The theoretical results in literature clearly deviate from the new experimental values. This implies that there is still space to perform high-level calculations for the state. Thus,

in this letter, PECs for the B¹Π state are calculated using multi-reference configuration-interaction method (MRCI)^[10,11] and large basis set. The large active space effect of core-valence correlation is emphasized. The PECs are fitted to the analytical potential energy functions (APEFs) for further analysis. The quality of the APEFs is evaluated by comparing the vibrational levels and the spectroscopic properties determined based on them with the available experimental values.

The PECs of B¹Π of KH are calculated with the internal contracted MRCI method. This is preceded by multi-configuration self-consistent-field calculations^[12,13] using C_{2v} symmetry. The basis sets ECP10MDF^[14] for K, which means that the electrons of 1s²2s²2p⁶ are described with pseudopotential, and the electrons of 3s²3p⁶4s¹ are described with basis sets (11s11p5d3f). For H, aug-cc-pVQZ basis set is used^[15].

To obtain high accurate interaction energy, three correlation schemes are performed for K. The first scheme includes the core electrons 3s²3p⁶. The second includes the core electrons 3p⁶, and the third includes only the valence 4s¹. Two different sets of active spaces (including 3d orbitals) are used. To show the calculation schemes clearly, we have listed the options for the two sets in Table 1. All calculations are performed using the MOLPRO 2009.1 program package^[16].

Each PEC includes 200 *ab initio* points with internuclear distances from 0.12 to 1.115 nm and a step of 0.005 nm. The PECs are subsequently fitted into the APEFs in the form of Murrell-Sorbie (MS) potential energy function^[17]. The general MS function, formulations of the root mean square (RMS) error, and spectroscopic parameters, such as the equilibrium rotational constant (B_e), are the harmonic and anharmonic constants (ω_e and $\omega_e\chi_e$) and the vibration-rotation coupling constant (α_e) that can be found in previous works^[18–26]. The vibrational levels are obtained by solving the radial Schrödinger equation for the bound and quasibound levels. The calculations are realized using the Le Roy's level

program package^[27].

As shown in Fig. 1, the dissociation energy (D_e) rapidly decreases from $X^1\Sigma^+$ to $B^1\Pi$. Thus, the potential wells become shallower; for $B^1\Pi$, the well is only “skin-deep”.

Based on the PECs, the APEFs are deduced using the MS function and the nonlinear least-square fitting method. The fitted parameters and the RMS for $B^1\Pi$ are listed in Table 2. The RMSs are small enough and thus, it can be regarded that the present APEFs can provide accurate spectroscopic properties for the states. To analyze further these characters quantitatively, the spectroscopic parameters based on the APEFs as well as the experimental values are presented in Table 3.

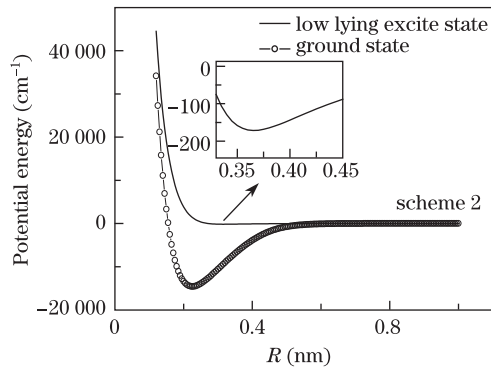


Fig. 1. PECs of the ground $X^1\Sigma^+$ and excited $B^1\Pi$ states of KH molecule derived using scheme 2.

Table 1. Computational Schemes Used in This Letter

Scheme	Correlated Electrons	Closed Orbitals	Active Orbitals	Uncontracted Configurations
1	10	0, 0, 0, 0	5, 2, 2, 0	70055168
2	8	1, 0, 0, 0	6, 3, 3, 0	75300796
3	8	1, 0, 0, 0	4, 2, 2, 0	5505740
4	2	2, 1, 1, 0	5, 2, 2, 0	2687
5	2	2, 1, 1, 0	3, 1, 1, 0	2687

Table 2. Fitted Parameters of MS for the $B^1\Pi$ State of KH (a_i in $(\text{nm}/10)^{-i}$)

$B^1\Pi$	Scheme 1	Scheme 2	Scheme 3	Scheme 4	Scheme 5
a_1	2.3171	2.6723	2.4193	1.4304	1.0263
a_2	0.4487	1.2039	0.8033	-0.9336	-1.4587
a_4	0.2338	0.7220	0.6829	0.7802	1.3871
a_4	0.1330	0.5032	0.5065	-0.2988	-0.7391
a_5	0.1198	0.1665	0.1881	0.1112	0.2026
a_6	0.0691	0.0157	0.0281	-0.0375	-0.0140
a_7	-0.0046	0.0024	-0.0071	0.0112	-0.0050
a_8	-0.0060	0.0051	-0.0014	-0.0018	0.0011
a_9	0.0011	0.0016	0.0008	0.0001	-6×10^{-5}
RMS	1.0	1.5	3.6	0.3	2.3

Table 3. Spectroscopic Parameters for the $B^1\Pi$ State of KH

	D_e	R_e	B_e	ω_e	$\omega_e \chi_e$	α_e
Scheme 1	259.2	3.0468	1.8659	199.1	39.4	0.4
Scheme 2	171.4	3.1598	1.7475	167.6	47.3	0.4
Scheme 3	198.1	3.1505	1.7544	170.4	47.3	0.4
Scheme 4	95.1	3.4305	1.5193	113.3	42.0	0.5
Scheme 5	95.8	3.4221	1.5264	115.5	45.6	0.5
Ross <i>et al.</i> ^[32]	293.1	3.146		155.3		
Khelifi <i>et al.</i> ^[8]	801	2.8258		246.4		
Expt. ^[11]	185	3.345	1.5322	109.1		

Using the five schemes, the range of D_e s is 95.1–259.2 cm^{-1} . The values 171.4 and 198.1 cm^{-1} , obtained using schemes 2 and 3, respectively, are in excellent agreement with the experimental value of 185 cm^{-1} ^[9]. Moreover, the values are considerably better than the theoretical values of 293.1 and 801 cm^{-1} given by Ross *et al.*^[28] and Khelifi *et al.*^[8], respectively. Using schemes 2 and 3, the R_e s obtained are close to those of Ross *et al.* and better than those of Khelifi *et al.*. However, when using schemes 4 and 5, the results are much closer to the experimental values with deviations of approximately 0.0077 nm. The experimental spectroscopic parameters for $B^1\Pi$ are limited; only ω_e and B_e are derived. Similar to the experimental values derived by Ross *et al.* and Khelifi *et al.* using schemes 2 and 3, the ω_e of the present study has a certain distance with the experimental value of 109 cm^{-1} ^[9]. However, the results obtained using schemes 4 and 5 are significantly closer to those of the experiment. B_e is in the same case as ω_e . However, this does not mean that the present results obtained using schemes 2 and 3 are less significant. Further investigations reveal that the real factor is the different method employed to determine ω_e and B_e .

Based on the APEFs, the rotational levels $T(\nu, J)$ are calculated and compared with the experimental values. The RMSs between the theoretical and experimental values for $J'=1-7$ are also computed. The results are shown in Table 4. $T(\nu, J)$ are $B^1\Pi$ term energies, where the minimum point of $X^1\Sigma^+$ is defined as zero. Only the levels of $\nu=0$ are presented here. The RMS of scheme 2 or 3 for $J'=1-7$ is smaller than those of the rest of the schemes; the RMS of scheme 2 is the smallest. To compare the ro-vibrational levels with the experimental data more sensibly, the energy levels are fitted into a function with three Dunham-type coefficients as $T(0, J) = A_{00} + A_{01}[J(J+1) - 1] + A_{02}[J(J+1) - 1]^2$, which is the same as that used by Lee *et al.*^[9]. The results are presented in Table 5. The B_e , D_{rot} , and ω_e of schemes 2 and 3 in this letter are in excellent agreement with the experimental values, but those of schemes 4 and 5 are evidently smaller. Obviously, the case is different from what is shown in Table 3. If fitted in the same computational method as the experimental ro-vibration energy levels, the levels achieved in this letter, which are based on the APEFS of schemes 2 and 3, can produce spectroscopic parameters which are in excellent agreement with the experimental values. Clearly, the discrepancies

Table 4. Ro-Vibrational Levels (cm⁻¹) of the B¹Π State

<i>J</i>	Scheme 1	Scheme 2	Scheme 3	Scheme 4	Scheme 5	Expt. ^[9]
	<i>T</i> (0, <i>J</i>)	<i>T</i> (0, <i>J</i>)	<i>T</i> (0, <i>J</i>)	<i>T</i> (0, <i>J</i>)	<i>T</i> (0, <i>J</i>)	<i>T</i> (0, <i>J</i>) ^[9]
0	28108.03	27456.38	28054.89	25960.97	25939.11	
1	28111.32	27459.31	28057.86	25963.20	25941.48	27684.13
2	28117.89	27465.16	28063.78	25967.62	25946.17	27690.27
3	28127.69	27473.87	28072.58	25974.16	25953.11	27699.25
4	28140.66	27485.34	28084.20	25982.69	25962.14	27711.29
5	28156.70	27499.46	28098.49	25992.98	25973.04	27726.02
6	28175.70	27516.05	28115.29	26004.64	25985.41	27743.37
7	28197.51	27534.85	28134.37	26016.53	25998.36	27763.12
8	28221.91	27555.45	28155.38			
9	28248.62	27576.99	28177.80			
10	28277.21		28200.64			
11	28306.85		28221.68			
12	28336.37					
RMS	430.01	226.20	372.73	1730.83	1751.12	

Table 5. Three Dunham-type Coefficients for the B¹Π State and the Molecular Constants Calculated from the Coefficients

	<i>A</i> ₀₀	<i>A</i> ₀₁ = <i>B</i> _e	<i>A</i> ₀₂ = <i>D</i> _{rot}	$\omega_e = \sqrt{4B_e^3/D_{rot}}$	<i>D</i> ₀
Scheme 1	28109.668	1.64913	-0.00094	138.2	190.1
Scheme 2	27457.824	1.47480	-0.00135	97.5	122.7
Scheme 3	28056.360	1.49045	-0.00131	100.5	147.9
Scheme 4	25961.921	1.15540	-0.00292	46.0	72.1
Scheme 5	25940.169	1.21570	-0.00284	50.3	70.7
Expt. ^[9]	27682.657	1.5322	-0.001203	109.1	131.4

are the result of the different computational methods. Since the validity of the method using the derivatives of APEF to compute spectroscopic parameters has been confirmed for numerous molecules^[18–26], the difference implies that the method which determines ω_e and *B*_e from the Dunham-type coefficients fitted with ro-vibrational levels is relatively inaccurate.

The ro-vibrational transitions are also used to test the reliability of the APEFs. The computational *P*, *R*, and *Q* based on the APEFs using scheme 2 or 3 for *J'* = 1–7 between $\nu = 0$ of B¹Π and $\nu = 0, 1$ of X¹Σ⁺ are determined and compared with the experimental transition frequencies^[9]. For brevity, they are not presented. To examine the transition frequencies for the rotational excited states, the experimental transition frequencies of *J'* = 1 are used as the baseline for the excited states. The RMSs for the errors between the experimental data and our results range from 0.1 to 0.95 cm⁻¹. This implies that the APEFs based on both schemes 2 and 3 can describe well the ro-vibrational spectra for the states. Schemes 2 and 3 are the satisfactory calculational policies in the investigation of the B¹Π of KH. Clearly, the active space has less effect on the molecular properties of KH than core-valence correlation.

In conclusion, the APEFs for the excited B¹Π state of KH are presented. Five computational schemes, which

include different valence electrons and active spaces, are employed. The spectroscopic parameters of the B¹Π state obtained with the derivative of APEFs and with the Dunham-type coefficients fitting are distinctly different because of the different computational method used. The transition frequencies are also obtained from the ro-vibrational levels, which are in excellent agreement with the experimental values. Based on the comparison between the present results and the experimental values, we conclude that the correlated electrons of 3p⁶4s¹ for K can provide satisfactory results in the derivation of the molecular properties of the B¹Π state for KH.

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