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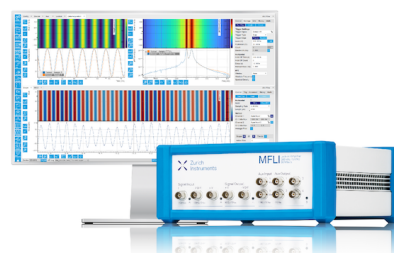
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Spectroscopic study of the $B^1\Pi$ state of ^{39}KH Ang-Yu Lee (李昂諭) and Wei-Tzou Luh (陸維作)^{a)}

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The $B^1\Pi$ excited electronic state of ^{39}KH has been observed for the first time by a pulsed fluorescence excitation spectroscopic technique. We have found only one vibrational level, in which seven e -parity and seven f -parity sublevels are identified. The Dunham-type coefficients A_{00} , A_{01} , and A_{02} and the mean internuclear separation for the $B^1\Pi$ state have been derived. Their numeric values are separately $27\,682.64(1)\text{ cm}^{-1}$, $1.533(1)\text{ cm}^{-1}$, $-0.001\,25(2)\text{ cm}^{-1}$, and $3.345(1)\text{ Å}$ for the $B^1\Pi^+$ state; $27\,682.66(2)\text{ cm}^{-1}$, $1.532(2)\text{ cm}^{-1}$, $-0.001\,20(3)\text{ cm}^{-1}$, and $3.347(2)\text{ Å}$ for the $B^1\Pi^-$ state. The dissociation energy D_0 is determined to be $131.4(7)\text{ cm}^{-1}$. The vibrational frequency and the dissociation energy for the $B^1\Pi$ state have also been estimated and the results are compared with recent *ab initio* calculations. © 2009 American Institute of Physics. [doi:10.1063/1.3250979]

I. INTRODUCTION

Potassium hydride has been the object of theoretical and spectroscopic interest since 1930s. However, up to now only the lowest two electronic states $X^1\Sigma^+$ and $A^1\Sigma^+$ have been identified and characterized by conventional spectroscopy,^{1–4} by laser spectroscopy,^{5–11} and by potential energy analysis,^{12–15} although some other electronic states have been predicted theoretically for more than 3 decades.^{16–23} The three lowest singlet potential energy curves are shown in Fig. 1, in which the potentials for the $X^1\Sigma^+$ and $A^1\Sigma^+$ electronic states are the Rydberg-Klein-Rees (RKR) curves,^{9,12,14} the potential for the $B^1\Pi$ state is an *ab initio* potential,²¹ and the dashed line denotes the energy of the asymptote $\text{K}(4^2P_{3/2}) + \text{H}(1^2S)$. Note that we did not portray the $A^1\Sigma^+$ RKR potential of Rafi *et al.*,⁴ which appeared to have six vibrational levels ($v=33\text{--}38$) lying energetically above the asymptote $\text{K}(4^2P_{1/2}) + \text{H}(1^2S)$, as noted also by Camacho *et al.*¹¹

Recently Khelifi *et al.*²³ performed an *ab initio* study for all electronic states below the ionic limit of KH. They also performed calculations²⁴ on dynamic couplings and radiative and nonradiative lifetimes of the $A^1\Sigma^+$ and $C^1\Sigma^+$ states of the KH molecule.

Partly due to the above theoretical predictions and partly due to our successful spectroscopic studies on the intriguing $\text{LiH } C^1\Sigma^+$ and $D^1\Sigma^+$ system,^{25–30} we have also carried out a spectroscopic study on the KH molecule. We first searched for the next high-lying singlet electronically excited state, which was predicted to be the $B^1\Pi$ electronic state.^{18,21,23}

In this article, we present the spectroscopic results on the excited $B^1\Pi$ electronic state of KH. By using a pulsed fluorescence excitation (FE) spectroscopic technique, we have observed seven e -parity and seven f -parity sublevels in the $v'=0$ state of this excited electronic state.

II. EXPERIMENT

One experimental setup is shown in Fig. 2. A frequency-doubled 10 Hz Q-switched Nd:YAG (yttrium aluminum garnet) laser (Quantel BW), having a pulse width of 4 ns and operating at a typical pulse energy of 40 mJ, was used to pump two different dye lasers (Lambda Physik FL3002 and Lumonics HD500). The Nd:YAG laser was regulated by a digital delay/pulse generator (Stanford DG535) for data management. The first dye laser beam, as a pump beam (PUMP), was used for a two-photon excitation of the potassium atom from its 4^2S state to its 6^2S state in order to produce the KH molecule from the reaction of $\text{K}(6^2S)$ with H_2 .³¹ A methanol solution of a laser dye LDS722 (exciton) was used as an active medium. The second dye laser was frequency doubled by a frequency-doubling system (Inrad autotracker III) in order to generate an ultraviolet laser beam as a probe beam (PROBE) for investigating the $B^1\Pi$ electronically excited state of KH. The methanol solutions of three laser dyes LDS722, LDS751, and LDS765 and their mixtures were used as active media. The laser pulse energy and the laser

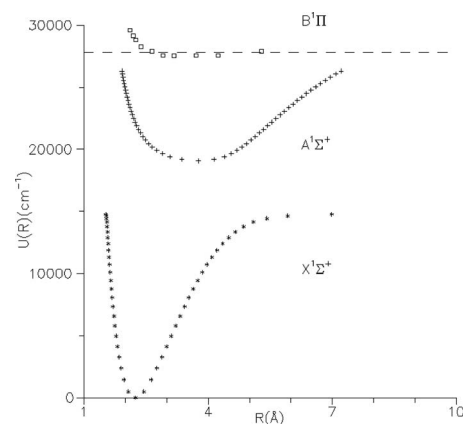


FIG. 1. Potential energy curves of KH: Two RKR curves for the $A^1\Sigma^+$ (pluses) and $X^1\Sigma^+$ states (stars) (from Ref. 14) and an *ab initio* potential for the $B^1\Pi$ state (open squares) (from Ref. 21). The dashed line denotes the $\text{K}(4^2P_{3/2}) + \text{H}(1^2S)$ asymptote. $U(R)$ in cm^{-1} and R in angstrom.

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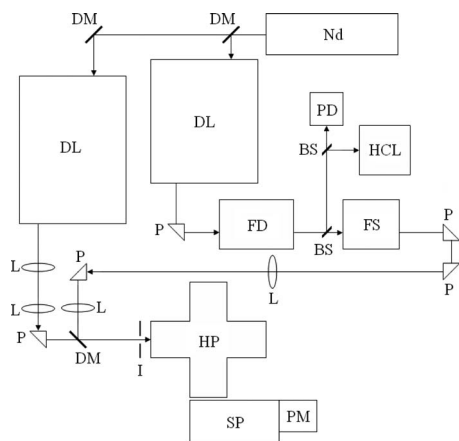


FIG. 2. Experimental setup. BS: A beam splitter; DL: A dye laser; DM: A dichroic mirror; FD: A frequency-doubling system; FS: A frequency separator; HCL: A hollow cathode lamp; HP: A potassium heat-pipe oven; I: An aperture; L: A focusing lens; Nd: A Nd:YAG laser; P: A 90° prism; PD: A photodiode; PM: A photomultiplier tube; SP: A spectrometer. Note that the frequency-doubled laser beam is the PROBE beam.

linewidth were ~ 2 mJ and ~ 0.2 cm^{-1} for the PUMP beam and ~ 3 mJ and ~ 0.04 cm^{-1} for the PROBE beam before frequency doubling. The frequency of the PROBE beam was calibrated by an optogalvanic spectrum taken with an Ar-filled lithium hollow cathode lamp (Perkin Elmer). The uncertainty of frequency measurements is about 0.1 cm^{-1} . The two laser beams were aligned collinearly along the axis of the longer arms of a six-arm crossed heat-pipe oven. The ultraviolet PROBE pulse was set to have a 10 ns optical delay behind the PUMP pulse. The heat-pipe oven, containing 10 g of naturally abundant potassium metal (STREM, 3N) in its short bottom arm, was normally operated under 10 Torr of hydrogen gas and at the temperature of 500 K, corresponding to a potassium vapor pressure³² of 25 mTorr. Under these conditions, Liu and Lin³¹ demonstrated that the KH molecules resulting from the reaction of $\text{K}(6^2S)$ with H_2 may be produced among four vibrational levels $v''=0-3$ of the $X^1\Sigma^+$ state, particularly having a product ratio $[\text{KH}(v''=1)]/[\text{KH}(v''=0)]=\sim 0.5$. The potassium atomic fluorescence and the induced fluorescence of KH were observed perpendicular to the laser beams. The fluorescence was collected with a set of folding mirrors and a cylindrical lens, and directed into a spectrometer (ARC SP275), which has a maximum spectral bandwidth [full width at half maximum (FWHM)] of about 9 nm. The transmitted fluorescence was detected by a photomultiplier (Hamamatsu R3896) detector. The detector signal was fed into a boxcar-averager-gated-integrator system (SRS SR250); the averaged output was recorded by a personal computer.

In this work, three types of spectra were measured. The first one was the potassium 4^2S-6^2S two-photon excitation spectrum in which the PUMP beam was scanned while the potassium 6^2S-4^2P atomic fluorescence at 692.95 nm was monitored. It was taken only for the purpose of centering the PUMP laser beam on the 4^2S-6^2S two-photon transition.

The second one was the FE spectrum of KH in which the PROBE beam was scanned while the PUMP laser was fixed

at the potassium 4^2S-6^2S two-photon transition and the induced fluorescence was monitored at three different locations: 442, 475, and 512 nm.

The third one was a resolved fluorescence spectrum in which the spectrometer was scanned while the PUMP laser was fixed at the potassium 4^2S-6^2S two-photon transition and the PROBE laser was tuned to a particular KH $B(v',J')-X(v'',J'')$ transition. During our preliminary measurements, we used a setup different from the one presented in Fig. 2. In this setup, the PUMP laser beam was provided by the (Lumonics HD500) dye laser having a linewidth of ~ 0.04 cm^{-1} , pumped by the Nd:YAG (Quantel BW) laser described above, and the PROBE laser beam before frequency doubling was provided by the (Lambda Physik FL3002) dye laser having a linewidth of ~ 0.2 cm^{-1} , pumped by another Nd:YAG (Quantel BB) laser, and their pulse delay was regulated digitally. We found that at a longer pulse delay, the intensities of potassium atomic transitions became weaker due to faster atomic relaxation,³³ and the molecular fluorescence of KH became discernible. In Sec. III C, we have used the fluorescence spectrum to demonstrate our electronic and vibrational assignments in a complementary manner.

III. RESULTS AND DISCUSSION

A. Fluorescence excitation spectra

To assure that the KH molecules are indeed produced in the heat-pipe oven after the potassium 4^2S-6^2S two-photon excitation, we measured a FE spectrum in the range of 20 510–21 110 cm^{-1} , covering mainly the $A^1\Sigma^+(9)-X^1\Sigma^+(0)$ vibrational band of KH. The FE spectrum was taken by observing fluorescence at 504 nm, corresponding mainly to the $A(9)-X(1)$ vibrational band of KH. The spectral transitions were then identified using the known molecular constants of the $X^1\Sigma^+$ and $A^1\Sigma^+$ electronic states.^{9,12,14} After such a confirmation, we explored the $B^1\Pi$ electronic state.

Based on an accurate dissociation energy (D_e) of 14 772.7(± 0.6) cm^{-1} for the $X^1\Sigma^+$ state^{9,13,14} and the atomic energy (13 042.89 cm^{-1}) for the $4^2P_{3/2}$ state of the potassium atom,³⁴ the asymptote ($\text{K}(4^2P_{3/2})+\text{H}$) of the $B^1\Pi$ state is expected to be located energetically at 27 815.59(± 0.6) cm^{-1} . Among the theoretical studies on the $B^1\Pi$ state, Melius *et al.*¹⁸ predicted first in 1979 a shallow well of 16 cm^{-1} at $9.57a_0$; in 1987 Ross *et al.*²¹ predicted a dissociation energy (D_e) of 293.1 cm^{-1} at $5.945a_0$ (3.146 Å) and a vibrational constant (ω_e) of 155.31 cm^{-1} , and recently in 2002 Khelifi *et al.*²³ predicted a dissociation energy (D_e) of 801 cm^{-1} at $5.34a_0$ (2.826 Å) and a vibrational constant (ω_e) of 246.4 cm^{-1} , which was derived from their vibrational spacing. From the latest two predictions, the dissociation energy ($D_0 \equiv D_e - (1/2)\omega_e$) might be close to 216 or 678 cm^{-1} .

Assuming that the dissociation energy (D_0) is ~ 678 cm^{-1} , one may then observe FE spectra of KH in the spectral range (a) of 26 648–27 326 cm^{-1} if excited from the lowest rovibrational level ($v''=0, J''=0$) of the $X^1\Sigma^+$ state and (b) of 25 691–26 370 cm^{-1} if excited from the

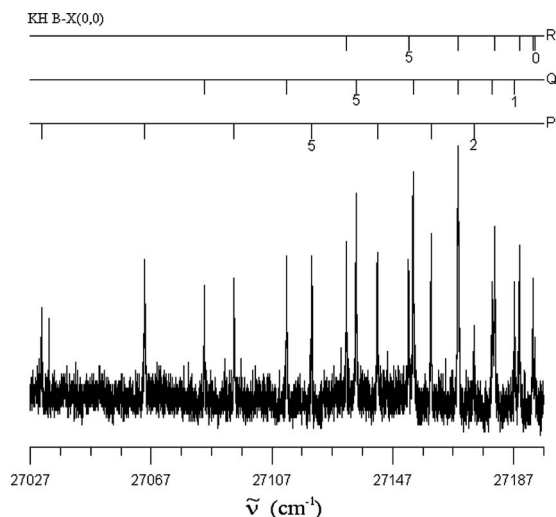


FIG. 3. Excitation spectrum of the $B^1\Pi-X^1\Sigma^+$ electronic transition of KH. The spectrum in the region of 27 027–27 197 cm^{-1} is excited from the $\nu''=0$ level of the $X^1\Sigma^+$ state.

rovibrational level ($\nu''=1$, $J''=0$). For case (a), FE transitions are only found in a narrow region of 27 027–27 197 cm^{-1} within the scanned range of 26 526–27 778 cm^{-1} . For case (b), FE transitions are also found in a limited region of 26 075–26 245 cm^{-1} within the scanned range of 25 876–26 600 cm^{-1} .

B. Spectral assignments

1. Excitation from $X^1\Sigma^+(0, J'')$ in the range of 27 027–27 197 cm^{-1}

Although the fluorescence was monitored at three different locations, 442, 475, and 512 nm, we obtained actually the same KH FE spectrum, except with different intensities, in the region of 27 027–27 197 cm^{-1} . The FE spectrum observed at 475 nm was found to be the most intense one and it is presented in Fig. 3, in which 21 discernible FE transitions have been identified. We have resolved these FE transitions into seven $P(2-8)$ transitions, seven $Q(1-7)$ transitions, and seven $R(0-6)$ transitions, respectively. Each e -parity sublevel is identified by (a) a simultaneous observation of P and R FE transitions as well as (b) the same resultant term energy within the uncertainty of 0.1 cm^{-1} . On the other hand, each f -parity sublevel was identified by (a) a term energy close to one of the e -parity sublevels that were already identified as well as (b) only one likely FE transition from each relevant rovibrational level ($0, J''$) of the ground $X^1\Sigma^+$ state, where the rotational levels are always of e -parity.³⁵

The term energy for each observed rovibrational level was obtained by adding the PROBE frequency together with the term energy of the relevant rovibrational level ($0, J''$), which was calculated with known ground-state constants G_0 , B_0 , and D_0 .⁹ Resultant term energies for these 14 sublevels and their spectral assignments are presented in the left-hand four columns of Table I, in which each UV transition frequency is an averaged value from four different measurements, and the number in parenthesis represents one standard deviation.

The observation of P , Q , and R transitions from each relevant rovibrational level ($0, J''$) of the ground $X^1\Sigma^+$ state is consistent with the selection rule ($\Delta\Lambda = \pm 1$, $\Delta J = 0, \pm 1$) for a $^1\Pi-X^1\Sigma^+$ electronic transition.^{35,36} The observation of only the line $R(0)$, without the lines $P(1)$ and $Q(0)$, indicates that the rotational level with $J'=0$ does not occur, and in turn that the value of the quantum number Λ' is of 1 for the upper electronic state. The above results demonstrate that the upper electronic state is a $^1\Pi$ state.

A plot of the resultant term energies $T(\nu', J')$ with respect to the value of $(J'(J'+1)-1)$ is presented in Fig. 4. From this figure, one can tell that all the observed term energies belong to the same vibrational level. Its absolute vibrational quantum number ν' is identified below by (a) a complementary FE spectrum out of the $\nu''=1$ level of the $X^1\Sigma^+$ state as well as (b) an observation of the intensity distribution for the ($B^1\Pi-X^1\Sigma^+$) ν' -band progressions with ν' in emission.

2. Excitation from $X^1\Sigma^+(1, J'')$ in the range of 26 075–26 245 cm^{-1}

Although the fluorescence was monitored at two locations, 440 and 475 nm, we obtained actually the same KH FE spectrum, except with different intensities, in the region of 26 075–26 245 cm^{-1} . The FE spectrum observed at 475 nm is presented in Fig. 5, in which 21 discernible FE transitions are also identified. Note that we can attribute each observed FE transition as an exciting transition from one relevant rovibrational level ($\nu''=1, J''$) of the $X^1\Sigma^+$ state to one of 14 sublevels (ν' , J' , e/f), which we have already identified in the 27 027–27 197 cm^{-1} region.

The term energy for each observed rovibrational level was also determined by adding the PROBE frequency together with the term energy of the relevant rovibrational level ($1, J''$) calculated with ground-state constants G_1 , B_1 , and D_1 .⁹ Resultant term energies for these 14 sublevels and their spectral assignments are presented in the right-hand four columns of Table I. From Table I, one can tell that (a) for each sublevel, except the sublevel $7e$ from the line $B-X(0,0)P(8)$, the term energies resulting from the two different spectral regions are consistent with one another within 0.2 cm^{-1} , and (b) there is only one vibrational level observed for the $B^1\Pi$ electronic state, although we did vary both the observing location and the initial ν'' level. The above results indicate that the $B^1\Pi$ electronic state may sustain only one vibrational level, whose absolute ν' value should be 0.

3. Molecular constants

The observed term energies were fitted into a set of three Dunham-type coefficients³⁷ in the equation $T(0, J') = A_{00} + A_{01}(J'(J'+1)-1) + A_{02}(J'(J'+1)-1)^2$. For the $B^1\Pi^+$ state, the Dunham-type coefficients A_{00} , A_{01} , and A_{02} are derived from 61 term energies for the seven e -parity sublevels and their numeric values are separately 27 682.636(14) cm^{-1} , 1.5333(13) cm^{-1} , and $-0.001\,250(24)$ cm^{-1} with an overall standard error of 0.049 cm^{-1} . Each parenthesized number represents one standard error for the last few digits. Note that for brevity, we

TABLE I. Observed FE transition frequencies and resultant term energies: (a) P and R transitions and (b) Q transitions. The first column lists the assigned FE transitions in the $B-X(0,0)$ band, and the last column those in the $B-X(0,1)$ band. $\nu_{\text{obs},0}$ are the observed FE frequencies (in cm^{-1}) from $v''=0$, and $\nu_{\text{obs},1}$ from $v''=1$; parenthesized numbers stand for one standard deviation in the last digit. $T(0,J',e/f)_0$ are the resultant term energies (in cm^{-1}) from $v''=0$, and $T(0,J',e/f)_1$ from $v''=1$; J' is the rotational quantum number.

(a) P and R transitions						
$B-X(0,0)$	$\nu_{\text{obs},0}$	$T(0,J',e)_0$	J'	$T(0,J',e)_1$	$\nu_{\text{obs},1}$	$B-X(0,1)$
$P(8)$	27 030.74(4)	27 762.89	7	27 763.32	26 081.36(2)	$P(8)$
$R(6)$	27 131.68(4)	27 763.17	7	27 763.20	26 179.37(2)	$R(6)$
$P(7)$	27 064.87(4)	27 743.37	6	27 743.51	26 113.85(2)	$P(7)$
$R(5)$	27 152.24(4)	27 743.39	6	27 743.47	26 198.97(2)	$R(5)$
$P(6)$	27 094.53(2)	27 726.02	5	27 726.20	26 142.37(4)	$P(6)$
$R(4)$	27 168.51(4)	27 726.00	5	27 726.05	26 214.38(2)	$R(4)$
$P(5)$	27 120.21(4)	27 711.36	4	27 711.38	26 166.89(2)	$P(5)$
$R(3)$	27 180.76(2)	27 711.30	4	27 711.33	26 225.93(2)	$R(3)$
$P(4)$	27 141.87(4)	27 699.36	3	27 699.36	26 187.69(2)	$P(4)$
$R(2)$	27 188.97(4)	27 699.29	3	27 699.31	26 233.63(2)	$R(2)$
$P(3)$	27 159.64(4)	27 690.18	2	27 690.37	26 204.97(2)	$P(3)$
$R(1)$	27 193.43(4)	27 690.26	2	27 690.24	26 237.71(4)	$R(1)$
$P(2)$	27 173.87(4)	27 684.19	1	27 684.28	26 218.60(2)	$P(2)$
$R(0)$	27 194.08(4)	27 684.16	1	27 684.19	26 238.24(8)	$R(0)$

(b) Q transitions						
$B-X(0,0)$	$\nu_{\text{obs},0}$	$T(0,J',f)_0$	J'	$T(0,J',f)_1$	$\nu_{\text{obs},1}$	$B-X(0,1)$
$Q(7)$	27 084.62(4)	27 763.12	7	27 763.28	26 133.62(2)	$Q(7)$
$Q(6)$	27 111.88(4)	27 743.37	6	27 743.59	26 159.76(2)	$Q(6)$
$Q(5)$	27 134.87(2)	27 726.02	5	27 726.06	26 181.57(2)	$Q(5)$
$Q(4)$	27 153.80(2)	27 711.29	4	27 711.37	26 199.70(2)	$Q(4)$
$Q(3)$	27 168.71(4)	27 699.25	3	27 699.44	26 214.04(6)	$Q(3)$
$Q(2)$	27 179.95(4)	27 690.27	2	27 690.33	26 224.65(4)	$Q(2)$
$Q(1)$	27 187.30(6)	27 684.13	1	27 684.17	26 231.64(4)	$Q(1)$

report each relevant value only up to the first nonsignificant digit in the abstract and tables. For the $B^1\Pi^-$ state, A_{00} , A_{01} , and A_{02} are derived from 31 observed term energies for the seven f -parity sublevels and their numeric values are sepa-

ately $27\,682.657(17)\text{ cm}^{-1}$, $1.5320(17)\text{ cm}^{-1}$, and $-0.001\,204(30)\text{ cm}^{-1}$ with an overall standard error of 0.048 cm^{-1} . Derived molecular constants are presented in Table II.

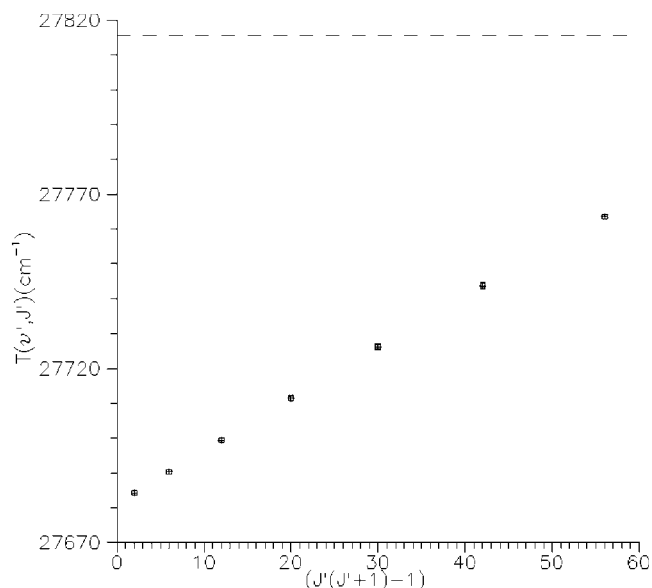


FIG. 4. A plot of the term energies $T(v', J')$ of the seven observed rovibrational levels with respect to the value of $(J'(J'+1)-1)$. The open squares denote the term energies for the e -parity sublevels and the pluses denote the f -parity sublevels.

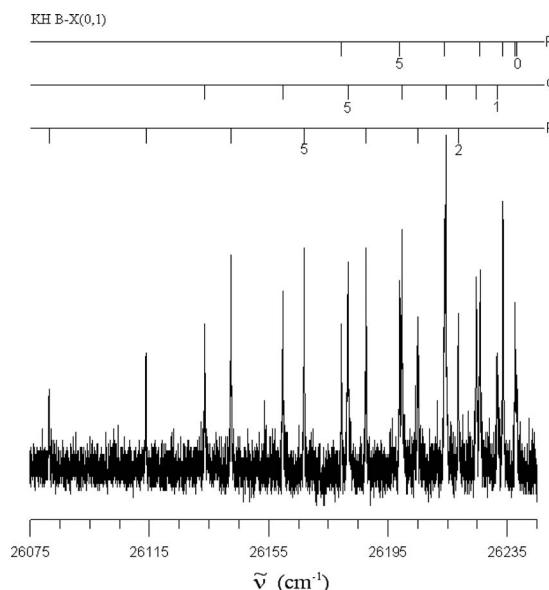


FIG. 5. Excitation spectrum of the $B^1\Pi-X^1\Sigma^+$ electronic transition of KH. The spectrum in the region of $26\,075\text{--}26\,245\text{ cm}^{-1}$ excited from the $v''=1$ level of the $X^1\Sigma^+$ state.

TABLE II. Molecular constants for the $B^1\Pi$ state of KH. $\langle R \rangle$ and R_e are in angstrom, and the other values are in cm^{-1} .

Constants	This work		Ross <i>et al.</i> ^a	Khelifi <i>et al.</i> ^b
	$B^1\Pi^+$	$B^1\Pi^-$		
A_{00}	27 682.64(1)	27 682.66(2)		
A_{01}	1.533(1)	1.532(2)		
$10^3 A_{02}$	-1.25(2)	-1.20(3)		
ω or ω_e	107.4(7)	109(1)	155.31	246.4
D_0	131.4(7)	131.4(7)		
D_e	185(1)	186(2)	293.1	801
$\langle R \rangle$ or R_e	3.345(1)	3.347(2)	3.146	2.826

^aReference 21.^bReference 23.

From the derived coefficient A_{01} and the reduced mass $\mu=0.982\,414\,34$ u for ^{39}KH ,¹⁴ the mean internuclear separation ($\langle R \rangle$) is determined to be $3.3453(11)$ Å for the $B^1\Pi^+$ state and $3.3467(15)$ Å for the $B^1\Pi^-$ state. The derived mean internuclear separations are presented (in four digits) in Table II together with recent theoretical equilibrium internuclear distances (R_e), 5.945 a.u. (3.146 Å) of Ross *et al.*²¹ and 5.34 a.u. (2.826 Å) of Khelifi *et al.*²³

By using the relation $D=4B^3/\omega^2$ and assuming that $B=A_{01}$ and $D=A_{02}$, we estimate the vibrational frequency (ω) to be $107.42(70)$ cm^{-1} for the $B^1\Pi^+$ state and $109.32(97)$ cm^{-1} for the $B^1\Pi^-$ state. These two values are presented in Table II together with recent theoretical ω_e values, 155.31 cm^{-1} of Ross *et al.*²¹ and 246.4 cm^{-1} of Khelifi *et al.*²³

By using averaged term energies, $27\,684.21(7)$ cm^{-1} for $T(0,1,e)$ and $27\,684.15(6)$ cm^{-1} for $T(0,1,f)$, and the asymptotic energy of $27\,815.59(60)$ cm^{-1} , the dissociation energy D_0 is determined to be $131.38(67)$ cm^{-1} for the $B^1\Pi^+$ state and $131.44(66)$ cm^{-1} for the $B^1\Pi^-$ state. If the zero-point energy is assumed to be $(\omega/2)$, then the dissociation energy D_e is estimated to be $185.1(1.4)$ cm^{-1} for the $B^1\Pi^+$ state and $186.1(1.6)$ cm^{-1} for the $B^1\Pi^-$ state. These two values are presented in Table II together with recent theoretical D_e values, 293.1 cm^{-1} of Ross *et al.*²¹ and 801 cm^{-1} of Khelifi *et al.*²³

The above results indicate that the $B^1\Pi$ state of KH is indeed a bound state, but its well is shallower than what two recent calculations had predicted.

C. $B^1\Pi-X^1\Sigma^+$ fluorescence

The above electronic and vibrational assignments can be also supported by the observed variation in intensity in a band progression in emission, which was actually taken during our preliminary experiments. In Fig. 6, part (a) portrays a portion of resolved fluorescence spectrum, observed by fixing the PROBE laser beam at 368.07 nm and at a time delay of 50 ns, and part (b) portrays assigned transitions with relevant Hönl-London line strengths³⁶ (in bars).

In the fluorescence spectrum, there are 15 discernible spectral peaks in the spectral range of $27\,020$ – $16\,930$ cm^{-1} . Two spectral peaks are attributed to the potassium atomic fluorescence: A truncated one ($K(4s-5p)$) near $24\,714$ cm^{-1}

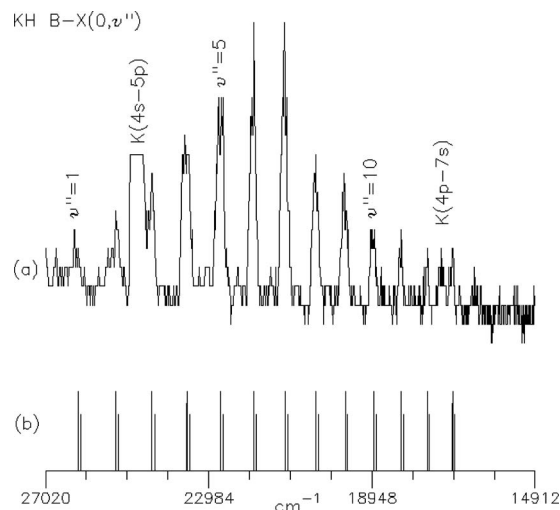


FIG. 6. Fluorescence spectrum of the $B^1\Pi-X^1\Sigma^+$ electronic transition of KH. (a) The region of $27\,020$ – $14\,912$ cm^{-1} from two rovibrational levels ($0,3f$) and ($0,5e$) of the $B^1\Pi$ state. Among 13 $B-X(0,v''=1-13)$ bands, only $v''=1, 5$, and 10 are denoted. $K(4s-5p)$ and $K(4p-7s)$ denote separately a truncated 4^2S-5^2P and a weak 4^2P-7^2S atomic fluorescence. (b) The height of each mark denotes a scaled Hönl-London line strength for one of the $Q(3)$, $R(4)$, and $P(6)$ transitions.

is due to the 4^2S-5^2P transition, and a weak one ($K(4p-7s)$) near $17\,251$ cm^{-1} due to the 4^2P-7^2S transition. Other spectral peaks can be interpreted below as the v'' -progression with $v'=0$ in emission.

Since we used a dye laser having a linewidth (FWHM) of about 0.2 cm^{-1} , the frequency-doubled PROBE beam would have a linewidth of about 0.4 cm^{-1} . If our above assignments are correct, then the PROBE laser beam at 368.07 nm may simultaneously excite both the $Q(3)$ and $R(4)$ transitions since their transition frequency difference is just about 0.2 cm^{-1} , and the two sublevels ($0,3,f$) and ($0,5,e$) of the B state may be simultaneously populated. The 39 fluorescent frequencies (in cm^{-1}) from these two excited sublevels down to the $v''=1-13$ levels can be easily found by taking the difference between their term energies and the relevant term energies of the X state, which were calculated with given and interpolated molecular constants.⁹ For each of the 13 $B-X$ bands, the relevant Hönl-London line strengths³⁶ for the emission lines $Q(3)$, $R(4)$, and $P(6)$ are also calculated, and the resultant line strengths are 1.75 , 1.5 , and 1.25 , respectively. Calculated fluorescent frequencies and relevant line strengths are presented (in bars) together in part (b) of Fig. 6. We found that calculated spectral transitions are lying band by band within observed fluorescence peaks in part (a). Such a good coincidence between observed fluorescence peaks of the v'' -progression and calculated fluorescent frequencies indicates that we are dealing with the $B-X$ emission, and in turn confirms again the electronic assignment of $B^1\Pi$.

The 13 observed $B-X$ fluorescence bands appeared only with a broad intensity maximum near $v''=6$ and 7 . The RKR outer turning points (R_{v^+}) for the $v''=6-8$ levels were found to locate separately at 3.2143 , 3.3203 , and 3.4258 Å.^{9,14} They (particularly R_{7^+}) are close to our derived mean internuclear separations of $3.3453(11)$ Å for the $B^1\Pi^+$ state and $3.3467(15)$ Å for the $B^1\Pi^-$ state. These results demonstrate

that we do deal with a ν' -progression with $\nu'=0$ in emission according to the Franck–Condon principle,³⁶ and in turn that the $\nu'=0$ assignment is indeed correct.

Note that a more complete comparison between the observed intensities with theoretical ones, like that for the $B^1\Pi$ state of LiH,³⁸ could not be performed since a potential, better than what is available presently, would be required for this. Note also that since the estimated vibrational frequency (ω) of 107.42(109.32) cm^{-1} is found to be smaller than the determined dissociation energy (D_0) of 131.38(131.44) cm^{-1} for the $B^1\Pi^+$ ($B^1\Pi^-$) state, one may expect that there may be other upper vibrational levels (particularly the $\nu'=1$ level) in the B state; however their Franck–Condon factors may be too small to have been observed in the present FE scheme.

IV. CONCLUSION

The $B^1\Pi$ state of ^{39}KH has been observed for the first time via a pulsed FE spectroscopic technique. Only one vibrational level has been observed with our spectral scheme. The electronic assignment is identified by (a) a simultaneous observation of P , Q , and R transitions, (b) the term energy region, and (c) a comparison between the fluorescence spectral peaks and the calculated transition frequencies in the ν' -progression. The $\nu'=0$ assignment is identified by (a) the observation of a single vibrational level and (b) the observation that the fluorescence bands of the ν' -progression appeared only with a broad intensity maximum. The Dunham-type coefficients and the mean internuclear separations for the $\nu'=0$ level and the dissociation energy (D_0) have been determined. The vibrational frequency (ω) and dissociation energy (D_e) for this electronic state are also estimated. The results are compared with recent theoretical calculations.

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