

Analysis of vibration–rotational spectra of KH¹

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Abstract

A modified Dunham potential model developed recently was applied to the analysis of vibration–rotational spectra of KH. The spectral data set consisted of 107 lines from the literature and an additional 12 lines measured in the present study. In total 119 spectral lines for four isotopomers were simultaneously fitted to a single set of only 11 molecular parameters, U_ω , U_B , a_1 , a_2 , a_3 , a_4 , a_5 , Δ_ω^H , Δ_B^H , r_0^H and Δ_{a1}^H , well within experimental errors. Values of $\omega_e(^{39}\text{KH})$ and r_e within the Born–Oppenheimer approximation are $986.6484(41) \text{ cm}^{-1}$ and $224.0164(10) \text{ pm}$, respectively, assuming that Δ_ω^K and Δ_B^K are equal to zero. © 1997 Elsevier Science B.V.

Keywords: KH; Vibration–rotational spectra; Born–Oppenheimer breakdown; Adiabatic; Nonadiabatic corrections

1. Introduction

High-resolution vibration–rotational spectra of diatomic molecules with infrared diode lasers or Fourier transform spectrometers provide many spectral lines for many vibrational states of various isotopomers. Simultaneous analysis of the spectral lines of all isotopomers by a least-squares fit to a single set of molecular parameters requires consideration of adiabatic and nonadiabatic corrections [1–6] to the Born–Oppenheimer approximation.

A conventional method of such analysis was to fit the spectral lines to the (v, J) levels of a molecule AB expressed in

$$E(v, J) = \sum_{i,j} \mu^{-(i+2j)/2} U_{ij} [1 + (m_e/M_a) \Delta_{ij}^a + (m_e/M_b) \Delta_{ij}^b] (v + 1/2)^i [J(J+1)]^j, \quad (1)$$

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which was given by Bunker [1] and was justified by Watson [2], in which U_{ij} and $\Delta_{ij}^{a,b}$ are the mass-invariant constants. The quantities M_a , M_b , and m_e are atomic masses of atoms A and B and the electron mass, respectively. μ is the reduced mass of molecule AB. U_{ij} and $\Delta_{ij}^{a,b}$ in Eq. (1) are the empirical parameters, which were originally introduced by Ross et al. [7] empirically to take into account the Born–Oppenheimer corrections.

Using Eq. (1), a least-squares fit of the spectral lines was typically made by treating all U_{ij} and Δ_{ij} as freely floating parameters in spite of the existence of the mutual constraints between U_{ij} parameters. Thompson et al. [8] proposed a model for the fit in which these constraints were taken into account. They introduced empirical parameters Δ_ω and Δ_B for ω_e and B_e , similar to Δ_{10} and Δ_{01} terms respectively, and analyzed the vibration–rotational and rotational lines in a least-squares fit to the Dunham potential energy parameters ω_e , B_e , a_1 , a_2 , a_3 , ... [9] and other Δ_ω and Δ_B . However, the model [8] did not work well

for light molecules for which the effect of the Born–Oppenheimer corrections were relatively large [10].

Ogilvie [5] succeeded in analyzing spectra of such light molecules by a fit to the potential parameters based on a Dunham formalism. He represented Δ_{ij} in terms of the adiabatic, nonadiabatic vibrational, and nonadiabatic rotational effects in a radial potential function with a perturbation treatment [11]. Although the potential model of Thompson et al. worked well for heavier molecules, for light molecules it needed to be modified algebraically by the introduction of expressions for Δ_ω and Δ_B and additional parameters representing the contributions of the adiabatic and nonadiabatic effects.

We analyzed the spectra of BrCl [12], GeS [13] and GeSe [14] using the model of Thompson et al. [8], which worked well for these massive molecules, and have recently made the modification [15] to apply the model to light molecules. A compact expression was given for the contributions for the Born–Oppenheimer corrections in the Hamiltonian to the Dunham's Y_{ij} coefficients. The modified potential model was applied to LiH and the vibration–rotational and rotational transitions of four isotopomers of LiH were fitted to a single set of molecular constants well within experimental error [15].

Potassium hydride is a typical light diatomic molecule that has a relatively large rotational constant. Haese et al. [16] observed the vibration–rotational spectra of $\nu = 1-0$ and $2-1$ bands of ^{39}KH and ^{41}KH isotopomers using a diode laser spectrometer. Subsequently Essig et al. [17] extended the measurements with a diode laser spectrometer to the same two bands for ^{39}KD . They [17] analyzed all spectral lines of the three isotopomers of KH simultaneously to determine a set of mass-invariant constants, U_{ij} and Δ_{ij}^H , which were treated in the fit as freely floating parameters.

The purpose of the present paper is to apply, to the vibration–rotational spectral lines of KH, our method of analysis of Δ_ω and Δ_B [15], which takes into account the mutual constraints between U_{ij} . Several newly measured lines of ^{39}KD and ^{41}KD were added to the previously reported set of spectral lines of KH [16,17]. A set of molecular constants for KH, which is sufficient for describing the spectral lines of four isotopomers, has been determined.

2. Method of analysis

The present method of analysis was reported previously [15] and here only the outline is given. We started from the effective Hamiltonian given by Watson [2] for a rotating and vibrating diatomic molecule. With an effective Hamiltonian, the Schrödinger equation can be written in terms of a variable $\xi = (r - r_c)/r_c$ as

$$\left[-\frac{h^2}{8\pi^2\mu_c r_c^2} \{1 + (m_e/M_a)Q_a(\xi) + (m_e/M_b)Q_b(\xi)\} \frac{d^2}{d\xi^2} + \frac{h^2}{16\pi^2\mu_c r_c^2} \{(m_e/M_a)Q_a''(\xi) + (m_e/M_b)Q_b''(\xi)\} + \frac{h^2}{8\pi^2\mu_c r_c^2 (1 + \xi)^2} \{1 + (m_e/M_a)R_a(\xi) + (m_e/M_b)R_b(\xi)\} J(J+1) + V(\xi) + (m_e/M_a)S_a(\xi) + (m_e/M_b)S_b(\xi) \right] \psi_{vJ}(\xi) = E_{vJ} \psi_{vJ}(\xi), \quad (2)$$

with

$$\mu_c^{-1} = (M_a + M_b - Cm_e)/M_a M_b. \quad (3)$$

The mass-independent functions $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, and $S_{a,b}(\xi)$, are the correction terms for the nonadiabatic vibrational, nonadiabatic rotational, and adiabatic effects, respectively [5]. C is the charge number of the molecule [2].

The Dunham potential energy function $V(\xi)$ [9] was expressed by

$$V(\xi) = (1/2)kr_c^2\xi^2(1 + a_1\xi + a_2\xi^2 + \dots). \quad (4)$$

After Ogilvie [5] functions $Q_{a,b}(\xi)$, $R_{a,b}(\xi)$, $S_{a,b}(\xi)$ were similarly expressed as Taylor expansions of ξ as

$$Q_{a,b}(\xi) = \sum_{i=0} q_i^{a,b} \xi^i, \quad (5)$$

$$R_{a,b}(\xi) = \sum_{i=0} r_i^{a,b} \xi^i, \quad (6)$$

$$S_{a,b}(\xi) = \sum_{i=1} s_i^{a,b} \xi^i. \quad (7)$$

The expansion coefficients $q_i^{a,b}$, $r_i^{a,b}$, and $s_i^{a,b}$ correspond to Ogilvie's coefficients $s_j^{a,b}$, $t_j^{a,b}$, and $u_j^{a,b}$, respectively, though he expanded the functions with the normalized internuclear distance $z[(r - r_c)/(r + r_c)]$.

A reduction of the Schrödinger Eq. (2) was necessary to obtain analytic expressions for Δ_ω and Δ_B algebraically. We assumed that the minimum of the effective potential function that consisted of $V(\xi)$ plus the adiabatic correction occurred at an internuclear distance r_c' and introduced a variable $\eta = (r - r_c')/r_c'$ so that the variable ξ became converted to η . Thus, we obtained a Schrödinger equation written in terms of a variable η , which was amenable to WKB treatment.

We calculated energy values using the WKB treatment [9] because the calculation was simple. It is known that both results for the energy level expressions derived from the WKB and perturbation approaches are the same [18]. The energy values F_{vJ} in wavenumber units were obtained as

$$F_{vJ} = \sum_{ij} Y_{ij}^{*vJ} (v+1/2)^j [J(J+1)]^j, \quad (8)$$

in which we used the notation Y_{ij}^{*vJ} to include the contributions from the Born–Oppenheimer correction terms to distinguish from Dunham's original notation Y_{ij} . The superscript vJ indicates that the Y_{ij}^{*vJ} coefficient includes the quantity F_{vJ} that is expressed as the polynomial of $(v+1/2)^j [J(J+1)]^j$.

Six Y_{ij}^{*vJ} values given in Ref. [15], selected for analysis of spectra, were

$$Y_{01}^{*vJ} = B_e^* + Y_{01}^{*vJ(2)} + \dots, \quad (9)$$

$$Y_{02}^{*vJ} = -(4B_e^{*3}/\omega_e^{*2})(1 - \delta r_1') + Y_{02}^{*vJ(2)} + \dots, \quad (10)$$

$$Y_{03}^{*vJ} = (16B_e^{*5}/\omega_e^{*4}) \left\{ 3 + k_1 - (5 + 3k_1/2)\delta r_1' + \delta r_2' \right\} + Y_{03}^{*vJ(2)} + \dots, \quad (11)$$

$$Y_{10}^{*vJ} = \omega_e^* (1 - \delta r_0'/2) + Y_{10}^{*vJ(2)} + \dots, \quad (12)$$

$$Y_{11}^{*vJ} = (B_e^{*2}/\omega_e^*) \left\{ 6(1 + k_1) - 3(1 + k_1)\delta r_0' - (4 + 3k_1)\delta r_1' + 2\delta r_2' \right\} + Y_{11}^{*vJ(2)} + \dots, \quad (13)$$

and

$$Y_{20}^{*vJ} = -(3B_e^*/8)(5k_1^2 - 4k_2)(1 - \delta r_0') + Y_{20}^{*vJ(2)} + \dots \quad (14)$$

in which

$$B_e^* = B_e \{ 1 + (m_e/M_a) \{ \Delta_B^a + (4B_e/\omega_e^2) q_1^a F_{vJ} \} + (m_e/M_b) \{ \Delta_B^b + (4B_e/\omega_e^2) q_1^b F_{vJ} \} \}, \quad (15)$$

$$\begin{aligned} \omega_e^* = \omega_e \{ & 1 + (m_e/M_a) \{ \Delta_\omega^a - (B_e/\omega_e^2)(3a_1 q_1^a - 2q_2^a) F_{vJ} \} \\ & + (m_e/M_b) \{ \Delta_\omega^b - (B_e/\omega_e^2)(3a_1 q_1^b - 2q_2^b) F_{vJ} \} \}, \end{aligned} \quad (16)$$

$$\begin{aligned} k_1 = a_1 \{ & 1 + (m_e/M_a) [\Delta_a^a - (2B_e/\omega_e^2) \\ & \times \{ (1 - 3a_1 + 4a_2/a_1) q_1^a + 2q_2^a - 2q_3^a/a_1 \} F_{vJ}] \\ & + (m_e/M_b) [\Delta_a^b - (2B_e/\omega_e^2) \{ (1 - 3a_1 + 4a_2/a_1) \\ & \times q_1^b + 2q_2^b - 2q_3^b/a_1 \} F_{vJ}] \}, \text{ etc.}, \end{aligned} \quad (17)$$

and

$$\delta r_i' = (m_e/M_a)(r_i^a - q_i^a) + (m_e/M_b)(r_i^b - q_i^b). \quad (18)$$

In eqns (9)–(14) we showed results for only the lowest-order terms $Y_{ij}^{*vJ(0)}$ because the effects of the Born–Oppenheimer corrections were negligible for $Y_{ij}^{*vJ(n)}$ coefficients where $n \geq 2$. The higher-order contributions $Y_{ij}^{*vJ(n)}$ ($n \geq 2$) in Eqs. (9)–(14) were assumed to have the same form as Dunham's $Y_{ij}^{(n)}$ ($n \geq 2$) values except that B_e , ω_e , a_1 , a_2 , ..., in $Y_{ij}^{(n)}$ ($n \geq 2$) were replaced by B_e^* , ω_e^* , k_1 , k_2 , ..., respectively. The Y_{ij}^{*vJ} values, other than those of Eqs. (9)–(14), were assumed to have the same form as the corresponding Dunham's Y_{ij} value.

3. Experimental

Spectra of KD were observed using a diode laser spectrometer equipped with a discharge cell of a White cell type. Gold-plated multireflection mirrors for the White cell were mounted at both ends of a 1 m long, 80 mm diameter glass tube with a gas inlet at one end and the outlet at the other. Molybdenum electrodes (2.5 cm outer diameter and 3.0 cm long) were placed at the gas inlet and the outlet portions. At the downstream section of the gas inlet, the glass cell tube, 20 cm in length, was heated using a wound resistance wire.

The White cell was incorporated into a tunable diode laser spectrometer, Spectra Physics (Laser Analytics) SP5000, using transfer optics and was set to 40 traversals, producing a 40 m optical path length in the cell. About 15 g of potassium was charged inside the glass tube at the heated zone, which was kept to $\approx 200^\circ\text{C}$. A gas mixture of 1.3 and 0.2 kPa of

He and D₂, respectively, was pumped continuously through the discharge cell using a mechanical pump (500 l/min). An ac discharge of peak to peak voltage of 5.3 kV was supplied at a frequency of 0.9 kHz. The discharge power dissipated by the gas was 320 W. KD was generated in a K + D₂ glow [16].

The full sweep, of typically 0.7 cm⁻¹, required 23 s with a time constant of 10 ms which was the smallest value available for our spectrometer. Since we eliminated high frequency noise by processing with Fourier transformations [19,20], large time constants were not required for phase-sensitive detection to observe the signals. Wavenumber calibration of the spectrum was made using the spectra of CO₂ [21] and acetylene [22]. Source modulated signals, at 1 kHz, of KD were observed in a wavenumber range between 676 and 735 cm⁻¹ using one laser diode.

4. Observed spectra and analysis

We transferred digitized diode laser spectra to a personal computer and processed all the spectra by Fourier transformation to eliminate high-frequency noise and fringes. Details of the processing have been reported previously [19,20]. Twelve spectral lines were assigned to the transitions which had not been reported before, 7 lines to the $\nu = 1-0$ band of ³⁹KD, 4 lines to the $\nu = 2-1$ band of ³⁹KD and one to the $\nu = 1-0$ band of ⁴¹KD. In Table 1 we list the 12 new lines and 107 lines reported previously by other authors [16,17]. The 107 reported lines are listed in the table to show Obs–Calc values in the present analysis. An outlier, P(16) of the $\nu = 1-0$ band of ³⁹KH, was excluded. Two transitions, R(5) and R(7) of the $\nu = 1-0$ band of ³⁹KD, are duplicated.

Analysis was made using Eqs. (9)–(14). Other Y_{ij} values and higher-order contributions to Eqs. (9)–(14) were taken from Bouanich [23], Woolley [24] and Ogilvie and Bouanich [25]. In total, 119 transitions for four isotopomers were fitted simultaneously to the modified potential [15] retaining 11 adjustable parameters, U_ω , U_B , a_1 , a_2 , a_3 , a_4 , a_5 , Δ_ω^H , Δ_B^H , $r_0'^H$ and Δ_{al}^H , in which

$$U_\omega = \omega_e \mu_c^{1/2}, \quad (19)$$

$$U_B = B_e \mu_c, \quad (20)$$

$$\Delta_\omega^{a,b} = \Delta_\omega^{ra,b} - r_0'^{a,b}/2, \quad (21)$$

and

$$r_i'^{a,b} = r_i^{a,b} - q_i^{a,b}. \quad (22)$$

These parameters were connected with the vibration–rotational energy levels through 19 Y_{ij}^{*vJ} values, i.e., $ij = 10, 20, 30, 01, 11, 21, 31, 02, 12, 22, 03, 13, 23, 04, 14, 05, 15, 06$ and 07 [4]. Atomic masses were taken from Audi and Wapstra [26].

We assumed errors of measurements to be 0.0010 cm⁻¹ and used equal weights for all the observed data. With the 11 parameters the fit converged after three iterations. The normalized standard deviation was 1.03, which corresponded to a standard deviation of 0.00103 cm⁻¹. The value of σ given by Essig et al. [17] was 0.0017 cm⁻¹ for the U_{ij} and Δ_{ij} fit.

5. Results and discussion

Using the present potential model we are able to fit the vibration–rotational spectra of four isotopomers of KH simultaneously with a single set of molecular parameters within experimental uncertainties. The standard deviation indicates that the quality of the fit is satisfactory. The molecular parameters determined in the present fit are shown in Table 2. Eq. (19) and Eq. (20) give U_ω and U_B in units of cm⁻¹ kg^{1/2} and cm⁻¹ kg, respectively, but we listed, in Table 2, the values of U_ω and U_B in cm⁻¹ u^{1/2} and cm⁻¹ u, respectively, converting kg to u [10,15]. Other parameters than those listed in Table 2 could not be determined and were set to zero in the fit.

From Eq. (9) and Eq. (12) we see $U_\omega = U_{10}$ and $U_B = U_{01}$, in which U_{10} and U_{01} are the terms given in Essig et al. [17]. Our values, 977.9344(41) cm⁻¹ u^{1/2} and 3.359209(29) cm⁻¹ u, for U_{10} and U_{01} are compared with their values, 977.9026(15) cm⁻¹ u^{1/2} and 3.359100(25) cm⁻¹ u [17], respectively. Essig et al. required 12 parameters to fit their KH data and obtained a value, 0.0017 cm⁻¹, for σ . However, we fitted almost the same and a slightly larger data set using 11 parameters getting the σ value of 0.0010 cm⁻¹.

The vibrational parameter $\omega_e = (1/2\pi c)(k/\mu_c)^{1/2}$ and the rotational parameter $B_e = h/(8\pi^2 \mu_c r_e^2 c)$, which are molecular parameters within the Born–Oppenheimer

Table 1

Vibration–rotational transition wavenumbers and Obs–Calc values of KH

v''^a	m^b	Obs (cm^{-1})	Obs – Calc (10^{-3} cm^{-1})	v''^a	m^b	Obs (cm^{-1})	Obs – Calc (10^{-3} cm^{-1})	v''^a	m^b	Obs (cm^{-1})	Obs – Calc (10^{-3} cm^{-1})
³⁹ KD (present study)				1	25	1027.3100	–0.85	0	–12	864.4602	–0.25
0	15	734.9885	0.41	1	23	1024.2570	0.68	0	–13	856.0120	–0.38
0	12	727.4463	1.49	1	21	1020.2540	2.36	1	18	1011.8800	–4.59
0	11	724.7815	0.13	1	20	1017.8980	–0.18	1	15	1002.1030	–0.05
0	9	719.2371	0.65	1	18	1012.5010	0.58	1	13	994.4920	2.77
0	8	716.3573	0.43	1	16	1006.1980	0.02	1	12	990.3650	1.83
0	7	713.4076	0.46	1	15	1002.7140	–0.07	1	11	986.0300	1.57
0	6	710.3889	0.66	1	14	999.0120	–0.08	1	8	971.8020	–2.23
0	3	680.2699	0.25	1	13	995.0940	–0.90	1	7	966.6650	–2.28
0	–4	676.6143	0.07	1	12	990.9650	–0.55	1	–2	912.2300	0.20
1	19	727.4782	0.73	1	11	986.6280	0.88	1	–7	876.2668	–1.00
1	17	723.2444	0.34	1	10	982.0820	–0.77	1	–11	844.9817	0.79
1	14	716.3152	1.02	1	9	977.3360	0.23	1	–12	836.8428	–0.07
1	10	706.0292	0.95	1	8	972.3880	–1.47	1	–13	828.5864	0.49
				1	7	967.2480	0.73				
⁴¹ KD (present study)				1	4	950.6810	0.51	³⁹ KD (Ref. [17])			
0	15	734.0841	1.15	1	3	944.7890	–1.22	0	21	747.9837	–0.37
				1	1	932.4810	1.12	0	14	732.5482	–0.87
³⁹ KH (Refs. [17, 16])				1	–2	912.7490	1.89	0	13	730.0326	1.75
0	19	1047.8750	3.54	1	–10	853.4380	–0.49	0	10	722.0451	0.16
0	18	1044.9380	0.71	1	–11	845.4121	–0.37	0	8	716.3558	–1.07
0	17	1041.7720	–1.89	1	–12	837.2641	0.45	0	6	710.3872	–1.04
0	16	1038.3850	1.07					0	4	704.1459	–0.92
0	15	1034.7700	–0.18	⁴¹ KH (Refs. [17, 16])				0	–7	665.3043	0.02
0	14	1030.9370	1.48	0	19	1047.2130	–1.13	0	–11	649.4619	0.10
0	13	1026.8820	–0.91	0	18	1044.2800	–0.88	0	–14	637.0442	–0.85
0	12	1022.6140	–1.41	0	17	1041.1190	0.16	0	–15	632.8109	1.00
0	11	1018.1350	–1.18	0	16	1037.7310	0.31	0	–16	628.5272	–1.18
0	10	1013.4460	–2.46	0	15	1034.1200	0.81	0	–17	624.2014	–0.15
0	9	1008.5590	3.45	0	14	1030.2860	–1.21	0	–18	619.8321	1.63
0	8	1003.4610	0.13	0	13	1026.2370	–0.70	0	–20	610.9595	–0.21
0	7	998.1650	–2.87	0	12	1021.9720	–1.73	1	20	729.4744	–1.36
0	6	992.6800	–0.10	0	11	1017.5000	1.56	1	14	716.3142	0.02
0	5	987.0020	0.84	0	10	1012.8140	–1.06	1	13	713.8525	–0.51
0	4	981.1370	2.30	0	9	1007.9270	0.11	1	12	711.3175	–0.20
0	3	975.0840	–0.44	0	8	1002.8380	0.66	1	9	703.2764	0.44
0	–1	949.1200	–1.39	0	7	997.5490	–0.85	1	8	700.4527	–0.48
0	–6	912.9940	–1.08	0	6	992.0710	3.04	1	–7	650.3238	0.42
0	–8	897.5040	0.19	0	5	986.3940	–1.27	1	–9	642.6370	–2.97
0	–9	889.5520	0.83	0	4	980.5380	2.58	1	–10	638.7193	–0.17
0	–10	881.4660	0.12	0	3	974.4910	–1.12	1	–11	634.7482	0.37
0	–11	873.2510	–0.94	0	2	968.2710	1.88	1	–15	618.3723	1.16
0	–13	856.4550	0.93	0	–6	912.4790	–0.37				
0	–14	847.8775	–0.59	0	–11	872.7877	–0.33				

^aFor transitions $\Delta v = v' - v'' = 1$.^b $m = J + 1$ and $m = -J$ respectively in the R and P branches.

Table 2
Dunham potential constants for KH

U_{ω} (cm ⁻¹ u ^{1/2})	977.9344(41) ^a
Δ_{ω}^H	-0.557(18)
U_B (cm ⁻¹ u)	3.359209(29)
Δ_B^H	-1.555(18)
r_0^H	1.63(45)
a_1	-2.20086(27)
Δ_{a1}^H	1.26(14)
a_2	3.05009(88)
a_3	-3.043(15)
a_4	1.963(51)
a_5	-0.60(11)

^aThe uncertainty (one standard error) in the last digits is given in parentheses.

approximation are calculated using Eq. (19) and Eq. (20) to be $\omega_e(^{39}\text{KH}) = 986.6484(41) \text{ cm}^{-1}$ and $B_e(^{39}\text{KH}) = 3.419341(30) \text{ cm}^{-1}$, respectively. Taking values of physical constants from the Green Book (1988) by Mills, Cvitas, Homann, Kallay and Kuchitsu [27] we obtain $r_e = 224.0164(10) \text{ pm}$, which is in contrast to the value, $r_e(^{39}\text{KH}) = 224.1152(16) \text{ pm}$, obtained by Haese et al. [16] from $Y_{01}(^{39}\text{KH})$. The value of r_e in the present analysis is the same for four isotopomers but it should be noted that the U_{ω} and U_B values have been determined assuming that the values of Δ_{ω}^K and Δ_B^K are equal to zero. Effects of Δ_{ω}^K and Δ_B^K on ω_e and B_e , respectively, will not be negligible. Therefore it is important to measure more extensively accurate transition frequencies for ^{39}K and ^{41}K isotopomers.

In conclusion, using a potential model [15] which was an extension of that proposed by Thompson et al. [8], all the spectral lines of the four isotopomers of KH were fitted to a single set of molecular constants simultaneously, well within experimental errors. Molecular parameters of KH within the Born–Oppenheimer approximation were extracted.

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