

The RKR Potential Energy Curves for the $X^1\Sigma^+$ and $A^1\Sigma^+$ States of KH^1

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New isotopically combined spectroscopic constants were obtained for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of KH/KD . These constants were used to construct new isotopically combined Rydberg–Klein–Rees (RKR) potential energy curves up to $v'' = 4$ of the $X^1\Sigma^+$ state and up to $v' = 26$ of the $A^1\Sigma^+$ state.

I. INTRODUCTION

Previous spectroscopic analysis of the $A^1\Sigma^+ - X^1\Sigma^+$ system of KH and KD consists of the following:

1. Almy and Hause (1) photographed KH in emission in the ~ 4100 - to $6600\text{-}\text{\AA}$ region. They reported the data on 27 bands that covered v'' from 0 to 4 and v' from 2 to 18 (correctly numbered; see item 5 below).

2. Hori (2) also photographed KH in emission and identified 62 bands, in particular, extending the upper state to $v' = 26$ (correctly numbered; see item 5 below).

3. Almy and Beiler (3) rephotographed KH in the 4150 - to $4650\text{-}\text{\AA}$ region and constructed an $A^1\Sigma^+$ "Klein's method" potential energy curve, i.e., what is now known as a Rydberg–Klein–Rees (RKR) potential. However, it is incorrect because of the incorrect vibrational numbering (see item 5 below).

4. Imanishi (4) analyzed the KD emission spectrum in the 4157 - to $6495\text{-}\text{\AA}$ region, but his analysis was apparently incorrect (see item 5 below).

5. Bartky (5) observed the absorption spectrum of KD in the 5100 - to $5200\text{-}\text{\AA}$ region and established the correct vibrational numbering for the $A^1\Sigma^+$ state (higher by 3 in KD than given by Imanishi (4) and higher by 2 in KH than given by Almy and Hause (1) and used by Hori (2) and Almy and Beiler (3)). In addition Bartky reanalyzed Imanishi's KD data (4) and Hori's KH data (2) to obtain a unified and correctly numbered set of rotational constants (B_v, D_v), band origins, and finally spectroscopic constants. The present analysis is based heavily on his analyses in particular.

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6. Cruse and Zare (6) briefly reported KH laser-excited fluorescence, but unfortunately K_2 absorption obscured the fluorescence doublets which correspond to $v'' > 4$, the observation of which would have allowed considerable extension of the ground-state potential (as was done in CsH (7) and RbH (8)).

The major reason for undertaking this work is to obtain accurate potential energy curves, e.g., for comparison with our $X^1\Sigma^+$ and $A^1\Sigma^+$ potential energy curves in LiH (9-12), NaH (13), RbH (8), and CsH (7). Additional reasons may be found elsewhere (9, 14).

In addition to the A-state RKR potential for KH noted above by Almy and Beiler (3), RKR potentials have been constructed by Jain and Sah (15) and by Numrich (16, 17), the latter unfortunately only in a thesis (16) (although a figure has appeared (17)). While all three $X^1\Sigma^+$ potentials should be reasonably accurate, only the Numrich potential (16) is valid for the $A^1\Sigma^+$ state because of the vibrational renumbering problem (5). Theoretical potential curves for KH have been calculated by Numrich and Truhlar (17), Laskowski and Stallcop (18), and Karo and Stevens (19). A careful comparison of the RKR and theoretical calculations for all alkali hydrides is under way at the University of Iowa and will be reported elsewhere.

We discuss the determination of improved isotopically combined spectroscopic constants in Section II. These improved constants are then used to obtain accurate Rydberg-Klein-Rees (RKR) potential energy curves in Section III.

II. ISOTOPICALLY COMBINED MOLECULAR CONSTANTS

The use of mass-reduced quantum numbers to determine average isotopically combined molecular constants (as opposed to ordinary single-isotope molecular constants (20)) has been extensively discussed, e.g., for HgH (21) and for several alkali hydrides (7, 10, 11, 22). The reduced masses (19) used in this work are

TABLE I

Rotational and Vibrational Spectroscopic Constants for the $X^1\Sigma^+$ State of KH

constant	isotopically combined ^a (this work)	Bartky ⁵	
		KH	KD (mass-reduced)
B_e	3.4126 ± 0.0017^b	3.4123 ± 0.0013	3.4189 ± 0.0031
α_e	0.0816 ± 0.0028	0.0817 ± 0.0010	0.0864 ± 0.0016
$\gamma_e \times 10^4$	3.4 ± 7.6	-	-
ω_e	985.24 ± 0.40	983.63 ± 0.57	986.54 ± 1.95
$\omega_e x_e$	14.92 ± 0.20	14.32 ± 0.10	15.07 ± 0.51
$\omega_e y_e$	0.088 ± 0.028	-	-

^a Non-rounded values (3.412619126, 0.0816744501, 0.0003447739, 985.2355137, 14.91533524, 0.0883553063) were used in the RKR calculation reported below, although that makes no significant difference in this case.

^b $R_e = 2.2424 \text{ \AA}$.

TABLE II

Rotational and Vibrational Spectroscopic Constants for the $A^1\Sigma^+$ State of KH

constant	isotopically combined ^a	Bartky ⁵	
		KH	KD (mass-reduced)
B_e	1.2119 ± 0.0115^b	1.269 ± 0.011	1.284 ± 0.023
α_e	-0.0665 ± 0.0041	-0.00375 ± 0.00029	-0.00346 ± 0.00079
γ_e	-0.00688 ± 0.00050	-	-
$\epsilon_e \times 10^4$	2.58 ± 0.25	-	-
$\phi_e \times 10^6$	-3.80 ± 0.43	-	-
ω_e	222.74 ± 0.16	228.23 ± 0.90	224.92 ± 1.26
$\omega_e x_e$	-7.169 ± 0.151	-5.75 ± 0.13	-6.35 ± 0.12
$\omega_e y_e$	-0.313 ± 0.013	-0.1693 ± 0.0055	-0.072 ± 0.002
$\omega_e z_e$	5.61 ± 0.52	-	-
$\omega_e a_e$	-4.87 ± 0.77	-	-

^a Non-rounded values (1.211900282 , -0.0665077733 , -0.0068767213 , 2.580463×10^{-4} , -3.80005×10^{-6} , 222.74135 , -7.16946996 , -0.3129870308 , 5.6141654×10^{-3} , $-4.8714908 \times 10^{-5}$) were used in the RKR calculation reported below. This is quite important for the highest levels since B_v and $G(v)$ values are the same order of magnitude as each of three positive and two negative terms. Thus the rounded constants do not provide an accurate representation for B_v and $G(v)$ functions near $v = 26$.

^b $R_e = 3.7629 \text{ \AA}$.

0.98241434 for ^{39}KH and 1.91510699 for ^{39}KD , based on the $^{12}\text{C} = 12$ scale. Thus $\mu(^{39}\text{KD}) = 1.94938827 \mu(^{39}\text{KH})$ and thus $\rho = (\mu(^{39}\text{KH})/\mu(^{39}\text{KD}))^{1/2} = 0.71622723$. In particular, one can fit experimental B_v and $G(v)$ data to the following Dunham-like expressions:

$$B_v = B_e - \alpha_e \eta + \gamma_e \eta^2 + \epsilon_e \eta^3 + \phi_e \eta^4, \quad (1)$$

$$\Delta G(v) = \left(\omega_e - \frac{1}{4} \omega_e y_e - \frac{1}{16} \omega_e a_e \right) + (-2\omega_e x_e + \omega_e z_e) \eta + \left(3\omega_e y_e + \frac{5\omega_e a_e}{2} \right) \eta^2 + (4\omega_e z_e) \eta^3 + (5\omega_e a_e) \eta^4, \quad (2)$$

where $\eta = v + 1/2$ for KH and $\eta = (v + 1/2)(0.716227)$ for KD, and the $\Delta G(v)$ values for KD are scaled (i.e., divided by 0.716227). $\Delta G(v)$ rather than $G(v)$ is fit to avoid the problem of relative zero-point energies. We have performed such fits for KH and KD data tabulated in Ref. (5). The B_v and $G(v)$ data are weighted inversely to the squares of the standard errors of the estimate given (5). Such fits reproduce the B_v and $\Delta G(v)$ data quite well for both isotopes; moreover, there are no sign correlations indicative of Born–Oppenheimer breakdown as found in the isotopic lithium hydrides (11) (although these latter data were more accurate). For the $X^1\Sigma^+$ state, the B_v and $\Delta G(v)$ fits employed only three constants (Table I). The average magnitude of the error (in cm^{-1})

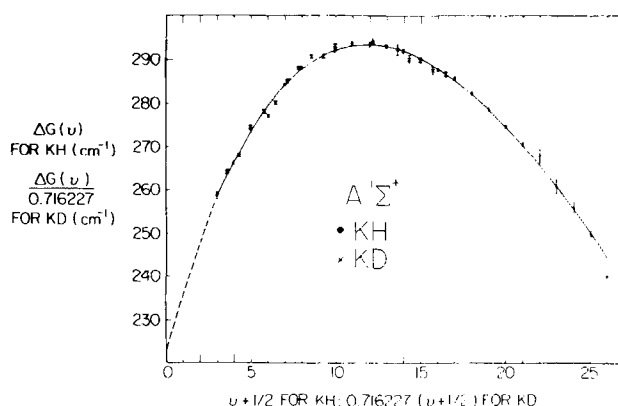


FIG. 1. The mass-reduced $\Delta G(v)$ plot for $A^1\Sigma^+$ KH and KD, showing our isotopically combined fit (—). Note the long extrapolation involved for low v' . Bartky's intercepts (presumably less accurate) would be 228.23 for KH and 224.92 for KD (5).

in B_v and $\Delta G(v)$ fits were 0.005 and 0.8 and the maximum errors 0.013 (for a ± 0.007 value) and 2.3 (for a ± 0.3 value), respectively. For the $A^1\Sigma^+$ state, all five constants were used (Table II). The average magnitudes of the error (in cm^{-1}) in the B_v and $\Delta G(v)$ fits were 0.004 and 0.5 and the maximum error 0.0335 (for a ± 0.0118 value) and 4.3 (for the last value ± 2.9). We give one example of these fits, the $\Delta G(v)$ fit for the $A^1\Sigma^+$ state, in Fig. 1. Note in particular the long extrapolation to $v + 1/2 = 0$. We believe these fits are superior to those given previously, e.g., by Bartky (5). In particular, five vibrational and five rotational constants are needed to represent the $A^1\Sigma^+$ -state data well.

III. ISOTOPICALLY COMBINED RKR

The empirical RKR turning points for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of KH were calculated using a computer program reported by Tellinghuisen (23). The results from using our rotational and vibrational spectroscopic constants in Tables I and II, for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states, respectively, are given in Tables III and IV and

TABLE III
Isotopically Combined RKR Potential Energy Curve of the $X^1\Sigma^+$ State of KH

v	$G(v) + Y_{00}$ (cm^{-1})	$R_-(\text{\AA})$	$R_+(\text{\AA})$
v_{\min}	0.00	2.2424	
$-\frac{1}{2}$	0.22	-	-
0	489.12	2.0714	2.4470
1	1444.81	1.9639	2.6229
2	2371.47	1.8975	2.7593
3	3269.62	1.8478	2.8808
4	4139.80	1.8076	2.9945

TABLE IV

Isotopically Combined RKR Potential Energy Curve of the $A^1\Sigma^+$ State of KH

v	$G(v) + Y_{00} \text{ (cm}^{-1}\text{)}$	$R_-(\text{\AA})$	$R_+(\text{\AA})$
v_{\min}	0.00	3.7629	
$-\frac{1}{2}$	2.05	-	-
0^a	115.17	3.3629	4.1379
1^a	351.26	3.0772	4.3895
2	599.04	2.8942	4.5562
3	856.87	2.7570	4.6920
4	1123.26	2.6479	4.8122
5	1396.82	2.5582	4.9237
6	1676.28	2.4827	5.0301
7	1960.46	2.4183	5.1334
8	2248.28	2.3624	5.2350
9	2538.75	2.3136	5.3358
10	2830.97	2.2704	5.4362
11	3124.17	2.2319	5.5367
12	3417.44	2.1972	5.6377
13	3710.26	2.1657	5.7392
14	4001.95	2.1369	5.8416
15	4291.95	2.1104	5.9449
16	4579.74	2.0858	6.0494
17	4864.85	2.0629	6.1551
18	5146.85	2.0414	6.2624
19	5425.34	2.0212	6.3714
20	5699.94	2.0023	6.4825
21	5970.30	1.9845	6.5958
22	6236.09	1.9680	6.7118
23	6496.97	1.9528	6.8310
24	6752.62	1.9390	6.9538
25	7002.71	1.9268	7.0810
26	7246.90	1.9165	7.2134

^a Not observed.

shown in Fig. 2. We believe these potentials are the best available because of the superior representation provided by our constants.

The zero-point energy, zpe , associated with a given potential curve is obtainable from the spectroscopic data through the expression

$$zpe = G(0) + Y_{00},$$

where

$$G(0) = \frac{\omega_e}{2} - \frac{\omega_e x_e}{4} + \frac{\omega_e y_e}{8} + \frac{\omega_e z_e}{16} + \cdots$$

and Y_{00} is a Dunham correction (24)

$$Y_{00} = \frac{B_e}{4} + \frac{\alpha_e \omega_e}{12B_e} + \frac{\alpha_e^2 \omega_e^2}{144B_e^3} - \frac{\omega_e x_e}{4}$$

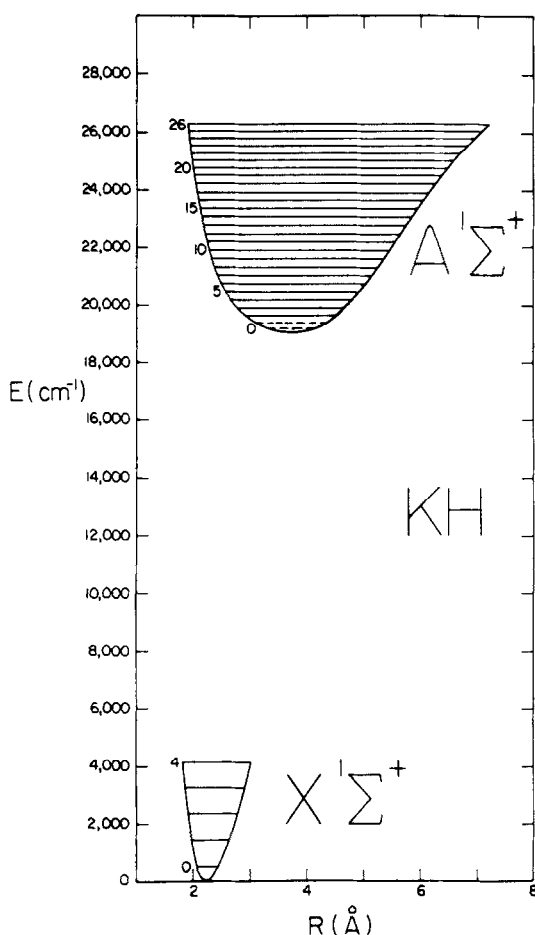


FIG. 2. The new isotopically-combined RKR potential energy curves (in cm^{-1} and \AA) for the $X'\Sigma^+$ and $A'\Sigma^+$ states of KH reported herein. Also shown as horizontal lines are the observed vibrational levels in the two potentials.

(note that the factor of 4 in the last term is missing in p. 109 of Ref. (24)). Using these equations and data from Tables I and II, the KH values calculated for Y_{00} , $G(0)$, and zpe , respectively, are 0.22, 488.90, and 489.12 cm^{-1} for the $X'\Sigma^+$ state and 2.05, 113.12, and 115.17 cm^{-1} for the $A'\Sigma^+$ state. For KD, they are 0.11, 350.92, 351.03 and 1.05, 80.67, 81.72 cm^{-1} , respectively. Analysis of these equations suggests that the uncertainty in zpe is $<1 \text{ cm}^{-1}$ for the $X'\Sigma^+$ state, but much greater ($\sim 10 \text{ cm}^{-1}$) for the $A'\Sigma^+$ state since the $v' = 0$ and 1 levels of KH and the $v' = 0-3$ levels of KD remain unobserved. Finally we note that our constants give $\nu_{00}(\text{KH}) = 18\,683 \text{ cm}^{-1}$, $\nu_{00}(\text{KD}) = 18\,788 \text{ cm}^{-1}$, and $\nu_e = 19\,057 \text{ cm}^{-1}$, although these values must be considered rather uncertain ($\sim 25 \text{ cm}^{-1}$) given the absence of low- v' data just noted.

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