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The $A^1\Sigma$–$X^1\Sigma$ Transition of ^{39}KH and ^{39}KD. Vibrational Numbering and Molecular Constants*

IAN R. BARTKY

Institute for Basic Standards, National Bureau of Standards, Washington, D. C.

The absorption spectrum of KD has been observed in the 5100–5200 Å region. An analysis of the spectrum in this region has shown that the previous assignments of the KD and KH spectra are in error. The v'-numbering of KD must be increased by 3, and the J-numbering of the P and R branches must be decreased by 1; the v'-numbering of KH must be increased by 2. Re-analysis of the existing data on KH and KD has given a consistent set of vibrational and rotational constants for the states of these molecules.

INTRODUCTION

The $A^1\Sigma$–$X^1\Sigma$ transition of KH has been studied by Almy and Hause (*1*) in absorption and emission, by Hori (*2*) in emission, and by Almy and Beiler (*3*) in emission. Imanishi (*4*, *5*) observed the emission spectrum of KD.

Herzberg (*6*) has stated that the correctness of Imanishi's analysis is in serious doubt. Briefly, the problems are: (1) unusual perturbations of all low J lines for all vibrational levels of the upper and lower states; (2) an electronic isotope shift of 20 to 40 cm^{-1}; (3) poor agreement between r_e (KH) and r_e (KD). Imanishi stated that on the basis of his analysis the v'-numbering for KH and KD was correct.

In an effort to resolve these problems, a study of KD was undertaken.

EXPERIMENTAL

A potassium sample with a stated purity of 99.95+ % was introduced, under vacuum, into a cast iron boat inside a 2-m stainless steel absorption tube. A furnace around the center, 50-cm section of the tube was heated to 650°C and the boat containing the potassium sample was pulled into the hot zone. Deuterium gas at a pressure of 700 torr was used to prepare the deuteride and to prevent too rapid diffusion of the potassium and the potassium deuteride formed at this temperature. The spectrum of KD was observed in absorption from 5100–5200 Å using a 35-ft, Eagle-mount spectrograph having a reciprocal dispersion of 0.75 Å/mm in the second order.

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Table I

Rotational constants for KD derived from Imanishi's data

Values in cm^{-1}

$v'v''$	0				1			
	B''_v	$10^5 D''_v$	B'_v	$10^5 D'_v$	B''_v	$10^5 D''_v$	B'_v	$10^5 D'_v$
4								
5								
6					1.700(6)	3.4(4)	.723(6)	2.6(4)
7					1.709(5)	4.3(4)	.728(5)	2.8(3)
8					1.706(6)	4.2(4)	.722(6)	2.4(4)
9					1.704(3)	4.1(2)	.730(3)	3.0(2)
10	1.743(15)	4.7(13)	.728(13)	2.8(12)	1.705(2)	4.0(2)	.735(4)	3.3(2)
11	1.749(17)	5.2(19)	.732(10)	2.8(10)	1.707(3)	4.0(2)	.730(2)	2.7(2)
12	1.758(16)	5.8(16)	.743(11)	3.9(10)	1.711(4)	4.5(3)	.729(4)	2.8(2)
13	1.748(13)	5.0(10)	.731(8)	3.2(6)				
14	1.750(12)	5.2(10)	.726(8)	2.9(8)				
15	1.745(12)	4.9(10)	.711(7)	2.2(6)				
16	1.743(5)	4.7(4)	.715(3)	2.7(2)				
17	1.740(7)	4.4(5)	.712(5)	2.9(4)				
18	1.741(9)	4.3(5)	.702(5)	2.3(3)				
19	1.740(8)	4.4(5)	.694(4)	2.3(2)				
20	1.743(6)	4.4(3)	.695(4)	2.4(2)				
21	1.738(4)	4.2(2)	.682(6)	2.1(3)				
22	1.736(7)	4.0(3)	.675(5)	1.9(2)				
23	1.736(5)	4.1(3)	.670(4)	2.2(2)				

TABLE I—*Cont.*

	2				3				4			
	B''_v	$10^5 D''_v$	B'_v	$10^5 D'_v$	B''_v	$10^5 D''_v$	B'_v	$10^5 D'_v$	B''_v	$10^5 D''_v$	B'_v	$10^5 D'_v$
4									1.610(5)	3.1(6)	.702(6)	2.4(6)
5					1.641(7)	4.0(5)	.712(5)	3.0(4)	1.617(2)	4.2(1)	.712(3)	2.8(1)
6					1.639(5)	3.5(3)	.718(3)	2.6(2)	1.610(4)	3.8(2)	.707(8)	2.2(3)
7	1.680(7)	4.3(7)	.726(6)	2.4(5)	1.633(5)	2.9(3)	.716(4)	2.1(3)				
8	1.678(11)	4.3(8)	.729(6)	3.0(4)	1.638(5)	3.4(2)	.728(3)	2.8(2)				
9	1.667(9)	3.6(7)	.725(5)	2.7(3)	1.631(4)	3.2(2)	.724(5)	2.4(2)				
10	1.670(3)	3.9(2)	.726(3)	2.6(2)								
11	1.672(4)	4.0(3)	.726(5)	2.6(3)								
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												

Table II

Observed and calculated origins for KD

Values in cm^{-1}

v',v''	0	1	2	3	4
4					16820.4(5) [20.7] {21.0}
					(189.1)
5				17653.9(2) (644.4) [53.6] {55.0}	17009.5(2) [08.9] {09.3}
				(192.1)	(191.8)
6		19179.4(2) [81.7] {82.6}		17846.0(2) (644.7) [45.8] {47.1}	17201.3(3) [01.1] {01.4}
		(198.7)		(195.3)	
7		19378.1(2) (674.5) [77.6] {78.2}	18703.6(2) (662.3) [01.9] {03.1}	18041.3(1) [41.7] {42.7}	
		(199.8)	(198.9)	(198.7)	
8		19577.9(2) (675.4) [76.7] {76.9}	18902.5(3) (662.5) [01.0] {01.8}	18240.0(2) [40.8] {41.4}	
		(200.9)	(201.0)	(199.8)	
9		19778.6(1) (675.1) [78.6] {78.4}	19103.5(2) (633.7) [03.0] {03.3}	18439.8(4) [42.7] {42.9}	
		(204.2)	(204.4)		
10	20675.2(5) (692.4) [74.1] {72.0}	19982.8(1) (674.9) [82.9] {82.2}	19307.9(2) [07.2] {07.1}		
	(207.5)	(206.1)	(207.6)		
	20882.7(7) (693.9)	20188.9(1) (673.3)	19515.5(6)		

TABLE II—*Cont.*

11	[50.3] {77.7}	[89.2] {87.9}	[13.5] {12.8}
	(206.1)	(208.3)	
	21088.8(4) (692.6)	20397.2(2)	
12	[88.0] {85.0}	[96.9] {95.2}	
	(208.3)		
13	21297.1(3)		
	(209.8)		
14	21506.9(4)		
	(213.2)		
15	21720.1(5)		
	(205.4)		
16	21925.5(2)		
	(210.5)		
17	22136.0(3)		
	(210.8)		
18	22346.8(4)		
	(209.4)		
19	22556.2(4)		
	(207.8)		
20	22764.0(3)		
	(207.5)		
21	22971.5(3)		
	(205.8)		
22	23177.3(3)		
	(205.3)		
23	23382.6(4)		

Legend Values in []: from KD data; values in {}: from KH data and isotope relations.

Table III

Rotational constants for KH derived from Hori's data

Values in cm^{-1}

v',v''	0				1			
	B''_v	$10^4 D''_v$	B'_v	$10^5 D'_v$	B''_v	$10^4 D''_v$	B'_v	$10^5 D'_v$
2								
3								
4					3.377(25)	2.45(27)	1.441(41)	16.6(48)
5	3.377(23)	1.61(23)	1.387(21)	8.6(20)	3.299(8)	1.62(7)	1.409(6)	10.4(7)
6	3.365(11)	1.38(15)	1.407(9)	7.7(13)	3.291(6)	1.58(5)	1.417(6)	10.3(6)
7	3.378(8)	1.54(13)	1.417(6)	7.4(10)	3.296(5)	1.61(5)	1.430(5)	11.1(5)
8	3.367(6)	1.44(7)	1.412(5)	8.5(5)	3.294(5)	1.60(4)	1.419(5)	10.2(4)
9	3.377(3)	1.65(3)	1.416(2)	10.6(3)	3.295(5)	1.60(4)	1.414(5)	9.9(3)
10	3.369(4)	1.53(3)	1.402(4)	9.5(3)	3.281(11)	1.50(9)	1.388(8)	8.6(6)
11	3.367(3)	1.49(2)	1.390(3)	9.1(2)				
12	3.370(2)	1.53(1)	1.380(3)	9.3(2)				
13	3.369(2)	1.52(3)	1.364(1)	9.0(1)				
14	3.369(3)	1.53(2)	1.348(2)	8.9(1)				
15	3.368(3)	1.53(2)	1.329(2)	8.5(1)				
16	3.374(3)	1.55(2)	1.318(3)	8.7(2)	3.290(11)	1.61(24)	1.317(11)	9.4(20)
17	3.376(2)	1.56(1)	1.303(2)	8.7(1)	3.290(10)	1.49(13)	1.303(7)	9.1(10)
18	3.377(3)	1.57(2)	1.276(2)	8.1(1)	[3.305]	[1.90]	1.264(22)	7.1(37)
19	3.366(3)	1.50(2)	1.252(3)	7.8(2)	3.265(25)	1.18(39)	1.238(15)	5.9(20)
20	3.376(5)	1.58(5)	1.240(4)	8.3(4)	3.293(7)	1.58(5)	1.239(15)	8.4(9)
21	3.365(5)	1.48(5)	1.215(6)	8.3(5)	3.255(14)	1.14(24)	1.174(18)	3.3(28)
22	3.333(28)	1.09(29)	1.166(24)	5.3(23)	3.284(14)	1.49(12)	1.168(14)	5.6(14)
23	3.335(30)	1.26(30)	1.115(21)	3.8(20)	3.297(13)	1.60(14)	1.166(12)	7.9(11)
24					3.260(11)	1.33(10)	1.102(12)	4.9(11)
25					3.283(8)	1.48(9)	1.094(5)	4.9(6)
26					3.289(43)	1.33(63)	1.115(34)	9.6(51)

TABLE III—*Cont.*

	2				3				4			
	B''_v	$10^4 D''_v$	B'_v	$10^5 D'_v$	B''_v	$10^4 D''_v$	B'_v	$10^5 D'_v$	B''_v	$10^4 D''_v$	B'_v	$10^5 D'_v$
2					3.122(10)	1.52(16)	1.333(8)	9.9(13)	3.010(48)	.13(293)	1.334(41)	9.6(203)
3	3.206(32)	1.45(37)	1.376(33)	10.6(35)	3.135(7)	1.61(8)	1.374(6)	10.3(7)	3.022(11)	1.25(25)	1.373(8)	12.1(16)
4	3.195(16)	1.35(17)	1.377(9)	8.9(8)	3.124(5)	1.52(5)	1.391(6)	10.2(5)	3.018(11)	1.23(21)	1.377(10)	7.2(17)
5	3.216(5)	1.59(4)	1.417(5)	11.3(4)	3.119(9)	1.48(9)	1.396(8)	9.2(8)	3.059(28)	3.31(135)	1.434(74)	27.1(394)
6	3.207(6)	1.54(5)	1.418(7)	10.6(6)	3.158(15)	1.85(15)	1.453(12)	13.1(11)	3.092(40)	6.00(231)	1.420(27)	14.4(137)
7	3.212(6)	1.58(5)	1.408(8)	8.7(6)	3.122(64)	1.57(65)	1.366(43)	5.3(48)				
8	3.206(17)	1.52(17)	1.406(14)	8.6(13)								
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20	[3.217]	[1.63]	1.191(38)	1.9(57)								
21	[3.684]	[9.28]	1.540(131)	59.9(187)								
22	3.201(21)	1.45(21)	1.203(21)	9.0(22)								
23	[3.188]	[3.72]	1.138(51)	22.0(300)								
24	3.303(89)	4.33(290)	1.186(67)	23.4(253)								
25	3.239(26)	2.19(43)	1.137(28)	11.6(44)								
26	3.197(10)	1.43(14)	1.068(8)	5.0(9)	3.169(23)	4.77(98)	1.124(17)	34.7(123)				

Table IV

Observed origins for KH

Values in cm^{-1}

v' \ v''	0	1	2	3	4
2				16389.8 (2) (871.6)	15518.2(17)
				(258.8)	(258.9)
3			17540.9 (51) (892.3)	16648.6 (3) (871.5)	15777.1 (2)
			(271.2)	(265.7)	(266.5)
4		18742.1(102) (930.0)	17812.1 (14) (897.8)	16914.3 (3) (870.7)	16043.6 (3)
		(269.6)	(273.2)	(272.7)	(275.1)
5	19971.3(32) (959.6)	19011.7 (6) (926.4)	18085.3 (3) (898.3)	17187.0 (3) (868.3)	16318.7 (2)
	(273.0)	(277.2)	(277.5)	(276.5)	(274.8)
6	20244.3 (4) (955.4)	19288.9 (2) (926.1)	18362.8 (3) (899.3)	17463.5 (4) (870.0)	16593.5 (9)
	(283.9)	(283.4)	(286.2)	(263.6)	
7	20528.2 (1) (955.9)	19572.3 (4) (923.3)	18649.0 (6) (921.9)	17727.1(64)	
	(288.0)	(288.4)	(284.2)		
8	20816.2 (1) (955.5)	19860.7 (2) (927.5)	18933.2 (18)		
	(290.6)	(290.7)			
9	21106.8 (1) (955.4)	20151.4 (4)			
	(292.1)	(290.8)			
10	21398.9 (1) (956.7)	20442.2 (7)			
	(293.5)				
11	21692.4 (1)				
	(293.0)				
12	21985.4 (1)				
	(292.9)				
13	22278.3 (0)				
	(291.5)				

TABLE IV—*Cont.*

14	22569.3 (1)				
	(290.0)				
15	22859.3 (1)				
	(287.5)				
16	23147.3 (1)	(954.9)	22192.4 (5)		
	(285.4)		(285.3)		
17	23432.7 (1)	(955.0)	22477.7 (4)		
	(282.4)				
18	23715.1 (1)		[22770.2]		
	(278.5)				
19	23993.6 (1)	(958.7)	23034.9(72)		
	(274.3)		(277.8)		
20	24268.4 (3)	(955.7)	23312.7 (7)		[22408.2]
	(270.3)		(273.2)		
21	24538.7 (5)	(952.8)	23585.9(16)		[22692.6]
	(268.9)		(266.8)		
22	24807.6(24)	(954.9)	23852.7(11)	(927.9)	22924.8 (35)
	(279.3)		(260.2)		
23	25087.4(92)	(974.5)	24112.9(12)		[23192.3]
			(255.5)		
24			24368.4 (4)	(918.4)	23450.0(149)
			(250.3)		(246.3)
25			24618.7 (4)	(922.4)	23696.3 (37)
			(242.1)		(238.5)
26			24860.8(47)	(926.0)	23934.8 (3) (900.1) 23034.7 (6)

Of the several bands of KD observed, one was analyzed in detail.[1] The results indicated: (1) no perturbations of the low J lines; (2) no electronic isotope shift; (3) good agreement between r_e (KH) and r_e (KD). The latter two results were obtained only when the v'-numbering of KH was increased by 2, and the v'-numbering of KD by 3.

KD MOLECULAR CONSTANTS

Imanishi's analysis for the rotational constants can be corrected if his J-values for the P and R branches are decreased by 1, all the perturbations vanishing with this re-assignment. His extensive data, rather than the data from our preliminary observations, were used to calculate the various constants. Minor misprints in his frequency tables were noted and corrected, and calculations were performed on an IBM 7094 computer using the NBS OMNITAB programs (*7*). In the following discussion, the new v'-numbering has been used, and the J-numbering has been corrected. All values given are in cm^{-1}.

The following equations (*6*)[2] were fitted to each band by the method of least-squares:

$$R(J) - P(J) = B_v'(4x) - D_v'(6x + 8x^3); \qquad x = J + \tfrac{1}{2}, \tag{1}$$

$$R(J-1) - P(J+1) = B_v''(4x) - D_v''(6x + 8x^3); \qquad x = J + \tfrac{1}{2}, \tag{2}$$

$$\begin{aligned} R(J-1) + P(J) = {} & \sigma_0(2) + (B_v' - B_v'')2x^2 \\ & - (D_v' - D_v'')\,(2x^2 + 2x^4); \qquad x = J. \end{aligned} \tag{3}$$

The results are shown in Tables I and II; the number immediately following the constant is the standard error of estimate by internal consistency (*8*), and applies to the last digit(s) of the constant. The values of B_v'' so obtained were weighted inversely as the square of the standard error of estimate and fitted to a polynomial in v''. The result was

$$B_v'' = (1.7539 \pm 0.0016) - (3.176 \pm 0.060) \times 10^{-2}(v'' + \tfrac{1}{2}). \tag{4}$$

The values of B_v' to $v' = 12$ were fitted similarly:

$$\begin{aligned} B_v' = {} & (0.659 \pm 0.012) + (1.27 \pm 0.29) \times 10^{-2}(v' + \tfrac{1}{2}) \\ & - (5.7 \pm 1.7) \times 10^{-4}(v' + \tfrac{1}{2})^2. \end{aligned} \tag{5}$$

The origins to $v' = 12$ were fitted in a similar manner:

[1] The frequencies are not listed here, since they are only slightly more accurate than the ones listed by Imanishi; however, high accuracy is not required: the analysis of this single band made it possible to discover the nature of Imanishi's error.

[2] Equations (1)–(3) are given in this form to indicate that B_v and D_v are obtained directly from the least-squares adjustment, rather than $(4B_v - 6D_v)$ and $8D_v$.

TABLE V

MOLECULAR CONSTANTS FOR THE $A^1\Sigma$–$X^1\Sigma$ TRANSITION OF ^{39}KH AND ^{39}KD
VALUES IN cm^{-1}

	KH	KD
σ_e	19 052.8 ± 2.1	19 059.9 ± 14.6
$\sigma_{0\text{-}0}$	18 680	18 789
ω_e'	228.23 ± 0.90	161.1 ± 5.2
$\omega_e'x_e'$	−5.75 ± 0.13	−3.25 ± 0.60
$10^2\omega_e'y_e'$	−16.93 ± 0.55	−7.2 ± 2.2
ω_e''	983.63 ± 0.57	706.6 ± 1.4
$\omega_e''x_e''$	14.32 ± 0.10	7.73 ± 0.26
B_e'	1.269 ± 0.011	0.659 ± 0.012
$10^2\alpha_e'$	−3.75 ± 0.29	−1.27 ± 0.29
$10^3\gamma_e'$	−2.32 ± 0.18	−0.57 ± 0.17
$10^5D_e'$ [a]	$9._5$	$2._7$
B_e''	3.4123 ± 0.0013	1.7539 ± 0.0016
$10^2\alpha_e''$	8.17 ± 0.10	3.176 ± 0.060
$10^4D_e''$ [a]	1.5_3	0.4_7 [b]
r_e' [c]	3.6_8 Å	3.6_6 Å
r_e'' [c]	2.24_2 Å	2.24_0 Å

[a] Graphical estimation, $D_v \sim D_e$.

[b] $\beta_e'' \sim -2.5 \times 10^{-6}$.

[c] The fundamental constants are from E. R. Cohen and J. W. DuMond, *Rev. Mod. Phys.* **37**, 537 (1965).

$$\sigma_0 = (19059.9 \pm 14.6) + (161.1 \pm 5.2)(v' + \tfrac{1}{2}) + (3.25 \pm 0.60)(v' + \tfrac{1}{2})^2 - (7.2 \pm 2.2) \times 10^{-2}(v' + \tfrac{1}{2})^3 - (706.6 \pm 1.4)(v'' + \tfrac{1}{2}) + (7.73 \pm 0.26)(v'' + \tfrac{1}{2})^2. \quad (6)$$

The last three figures of the calculated origins are given between the square brackets in Table II.

KH MOLECULAR CONSTANTS

It is difficult to assess the quality of Hori's data from his published calculations: (1) the rotational constants, which are averages over many bands, contain more significant figures than are justified by his data; (2) his formula for B_v'' as a function of v'' systematically deviates from the values of B_v'' he lists; (3) his Deslandres table of band origins is based on smoothed values, rather than on the experimentally determined origins.

His data were re-analyzed by the procedures outlined above. Minor misprints in the line identifications were noted and corrected. The results of the analysis are shown in Tables III and IV. The constants in square brackets are for bands

which have too few points to permit a least-squares solution. All values given are in cm^{-1}. The constants as a function of v are given by

$$B_v'' = (3.4123 \pm 0.0013) - (8.17 \pm 0.10) \times 10^{-2}(v'' + \tfrac{1}{2}); \tag{7}$$

$$B_v' = (1.269 \pm 0.011) + (3.75 \pm 0.29) \times 10^{-2}(v' + \tfrac{1}{2}) - (2.32 \pm 0.18) \times 10^{-3}(v' + \tfrac{1}{2})^2, \text{ to } v' = 12; \tag{8}$$

$$\begin{aligned} \sigma_0 = {} & (19052.8 \pm 2.1) + (228.23 \pm 0.90)(v' + \tfrac{1}{2}) \\ & + (5.75 \pm 0.13)(v' + \tfrac{1}{2})^2 - (1.693 \pm 0.055) \times 10^{-1}(v' + \tfrac{1}{2})^3 \\ & - (983.62 \pm 0.57)(v'' + \tfrac{1}{2}) \\ & + (14.32 \pm 0.10)(v'' + \tfrac{1}{2})^2, \text{ to } v' = 12. \end{aligned} \tag{9}$$

ISOTOPE RELATIONS

The simple isotope theory (*6*) adequately describes the various constants; $\rho = 0.71623$ for $^{39}KH - {}^{39}KD$.[3] In Table II in braces are given the last three digits of the band origins for KD calculated from Eq. (9) and the isotope relations.

SUMMARY

The molecular constants for KH and KD obtained from the re-analysis of Hori's and Imanishi's data are given in Table V. The agreement among the various constants is satisfactory.

This research has shown that it is necessary to observe the spectrum of KD in order to establish the upper-state vibrational numbering of KH unequivocally. Similar observations of NaD (*10*) were required to establish the v'-numbering of NaH.

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