

LETTER TO THE EDITOR

The Rydberg - Klein - Rees potential energy curve of the $A^1\Sigma^+$ state of KH

To cite this article: M Rafi *et al* 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** L533

View the [article online](#) for updates and enhancements.

You may also like

- [Deriving Color Transformations for VR/Photometry](#)
B. J. Taylor and M. D. Joner
- [Investigating the 2nd knee: The KASCADE-Grande experiment](#)
A Haungs, W D Apel, F Badea et al.
- [Thermodynamic Analysis of the Molten System KF - KCl - KBF₄ - K₂TiF₆](#)
V. Dank, M. Chrenková, A. Šilný et al.

LETTER TO THE EDITOR

The Rydberg–Klein–Rees potential energy curve of the $A^1\Sigma^+$ state of KH

M Rafi, Reem Al-Tuwirqi and Fayyazuddin

Physics Department, Faculty of Science, King Abdul Aziz University, Jeddah, Saudi Arabia

Received 19 April 1996

Abstract. New spectroscopic data have been used to extend the Rydberg–Klein–Rees potential energy curve of the $A^1\Sigma^+$ state of the KH molecule from $v = 27$ to 38.

The excited state $A^1\Sigma^+$ of each of the alkali hydrides has become of great interest to spectroscopists because of its anomalous behaviour. It is found that the vibrational energy intervals of this state increase with increasing v to a maximum and then begin to fall monotonically. The $A^1\Sigma^+ - X^1\Sigma^+$ system of alkali hydrides has been widely studied and in this regard a comprehensive review has been given by Stwalley *et al* (1993). Near dissociation spectra of $A^1\Sigma^+ - X^1\Sigma^+$ systems of LiH, NaH and KH have been reported by Rafi *et al* (1993). They have given the vibrational and rotational analysis of the newly observed bands and their data can be regarded as significant in extending the potential energy curve in the observed region of the $A^1\Sigma^+$ states of these molecules. In this letter we present calculations of the Rydberg–Klein–Rees (RKR) (1932, 1933, 1947) potential energy curve of the $A^1\Sigma^+$ state of the KH molecule from both previous data (Bartky 1966) and new data (Rafi *et al* 1993). Potential energy calculations by the RKR method on the $A^1\Sigma^+$ states of LiH and NaH from the data of Rafi *et al* (1993) are in progress.

The Rydberg–Klein–Rees (RKR) method (1932, 1933, 1947) is commonly used in the construction of accurate potential curves of the stable molecular states of diatomic molecules from the observed spectroscopic data of the vibrational and rotational energy levels. This method describes the evaluation of the turning points $R_{\min}(v, J = 0)$ and $R_{\max}(v, J = 0)$. It is well known that the turning points can be expressed as follows:

$$R_{\max}(v) = \left(\frac{f(v)}{g(v)} + f(v)^2 \right)^{1/2} + f(v) \quad R_{\min}(v) = \left(\frac{f(v)}{g(v)} + f(v)^2 \right)^{1/2} - f(v) \quad (1)$$

where

$$\begin{aligned} f(v) &= \left(\frac{\hbar}{4\pi c\mu} \right)^{-1/2} \int_{-1/2}^v [G(v) - G(x)]^{-1/2} dx \\ &= \frac{1}{2} (R_{\max}(v) - R_{\min}(v)) \\ g(v) &= \left(\frac{4\pi c\mu}{\hbar} \right)^{1/2} \int_{-1/2}^v B(x) [G(v) - G(x)]^{-1/2} dx \\ &= \frac{1}{2} \left(\frac{1}{R_{\max}(v)} - \frac{1}{R_{\min}(v)} \right). \end{aligned} \quad (2)$$

$B(x)$ and $G(x)$ are the rotational constant and vibrational energy for level x . The potential energy curve can thus be constructed from constants available from spectroscopic analysis. We have made use of the computer program of Le Roy (1992) in performing the RKR calculations in the present work.

Spectroscopic constants used in constructing the RKR curve of the $A^1\Sigma^+$ state of KH are worked out using Dunham-like expressions:

$$B(v) = \sum_{i \geq 0}^n Y_{i1}(v + 1/2)^i$$

$$= Y_{01} - Y_{11}(v + 1/2) + Y_{21}(v + 1/2)^2 + Y_{31}(v + 1/2)^3 + \dots \quad (3)$$

The observed $B(v)$ values are fitted to a polynomial in $(v + 1/2)$ by a least square fit program and the rotational constants are determined. The values of B_v for $v = 2$ to 26 are taken from the data of Bartky (1966) and those of $v = 27$ to 38 from the data of Rafi *et al* (1993) from their analysis of the $A^1\Sigma^+ - X^1\Sigma^+$ system of KH with $v'' = 1$. The vibrational constants are also determined from the Dunham-like expression:

$$G(v) = \sum_{i \geq 1}^n Y_{i0}(v + 1/2)^i$$

$$= Y_{10}(v + 1/2) - Y_{20}(v + 1/2)^2 + Y_{30}(v + 1/2)^3 + \dots \quad (4)$$

$G(v)$ values for $v = 0$ to 26 are built from Bartky's data (1966) and for $v = 27$ to 38 from the data of Rafi *et al* (1993). The constants of the $X^1\Sigma^+$ state for $v'' = 0$ and 1 have been taken from Hussein *et al* (1986) as recommended by Stwalley *et al* (1991) in building the $G(v)$ values. The least square fit program is used to determine the vibrational constants. Both the rotational and vibrational constants thus determined have been listed in table 1. Yang *et al* (1980) evaluated the isotopically combined rotational and vibrational constants of KH $A^1\Sigma^+$ state from the analysis of Bartky (1966). Pardo *et al* (1987) also reported isotopically combined constants of this state. However, Stwalley *et al* (1991) recommend the values of Yang *et al* (1980) and so we have given their values along with our values in table 1.

$$ZPE = G(0) + Y_{00} \quad (5)$$

Table 1. Spectroscopic constants of the $A^1\Sigma^+$ state of KH^a.

Constants	This work (cm ⁻¹)	Yang <i>et al</i> (1980) (cm ⁻¹)
Y_{10}	222.755 93	222.741 35
Y_{20}	7.007 966 98	7.169 469 96
Y_{30}	-0.285 188 846 2	-0.312 987 030 8
Y_{40}	0.004 127 397 6	0.005 614 165 4
$10^1 Y_{50}$	-0.000 235 891 66	-0.000 487 149 08
Y_{01}	1.219 076 147	1.211 900 282
$10^1 Y_{11}$	0.621 124 733	0.665 077 733
$10^1 Y_{21}$	-0.062 904 284	-0.068 787 213
$10^2 Y_{31}$	0.024 329 777	0.025 804 63
$10^2 Y_{41}$	-0.000 480 766	-0.000 380 005
$10^3 Y_{51}$	0.000 037 778 04	

^a Non-rounded values are used to construct the RKR potentials as these are quite significant for higher vibrational levels.

Table 2. RKR potential energy curve of the A $^1\Sigma^+$ state of KH.

v	$G(v) + Y_{00}(\text{cm}^{-1})$		$R_{\min} (\text{\AA})$		$R_{\max} (\text{\AA})$	
	$a \equiv \text{This work}$	$b \equiv \text{Yang et al (1980)}$	$a \equiv \text{This work}$	$b \equiv \text{Yang et al (1980)}$	$a \equiv \text{This work}$	$b \equiv \text{Yang et al (1980)}$
v_{\min}	0.00	0.00	3.7526	3.7629	3.7526	3.7629
$-1/2$	1.84	2.05	—	—	—	—
0^a	114.94	115.17	3.3515	3.3629	4.1331	4.1379
1^a	350.80	351.26	3.0706	3.0772	4.3873	4.3895
2	598.24	599.04	2.8905	2.8942	4.5565	4.5562
3	855.72	856.87	2.7553	2.7570	4.6938	4.6920
4	1121.82	1123.26	2.6474	2.6479	4.8149	4.8122
5	1395.20	1396.82	2.5584	2.5532	4.9267	4.9237
6	1674.62	1676.28	2.4833	2.4827	5.0328	5.0301
7	1958.90	1960.46	2.4190	2.4183	5.1356	5.1334
8	2246.95	2248.28	2.3631	2.3624	5.2365	5.2350
9	2537.77	2538.75	2.3140	2.3136	5.3364	5.3358
10	2830.43	2830.97	2.2706	2.2704	5.4360	5.4362
11	3124.05	3124.17	2.2317	2.2319	5.5358	5.5367
12	3417.85	3417.44	2.1968	2.1972	5.6362	5.6377
13	3711.09	3710.26	2.1651	2.1657	5.7374	5.7392
14	4003.13	4001.95	2.1362	2.1369	5.8397	5.8416
15	4293.35	4291.95	2.1096	2.1104	5.9433	5.9449
16	4581.21	4579.74	2.0851	2.0858	6.0484	6.0494
17	4866.22	4864.85	2.0624	2.0629	6.1550	6.1551
18	5147.94	5146.85	2.0412	2.0414	6.2634	6.2624
19	5426.00	5425.34	2.0213	2.0212	6.3736	6.3714
20	5700.04	5699.94	2.0027	2.0023	6.4857	6.4825
21	5969.77	5970.30	1.9851	1.9845	6.5999	6.5958
22	6234.94	6236.09	1.9685	1.9680	6.7163	6.7118
23	6495.32	6496.97	1.9529	1.9528	6.8349	6.8310
24	6750.75	6752.62	1.9380	1.9390	6.9559	6.9538
25	7001.06	7002.71	1.9240	1.9268	7.0793	7.0810
26	7246.13	7246.90	1.9107	1.9165	7.2053	7.2134
27	7485.89		1.8982		7.3339	
28	7720.24		1.8865		7.4653	
29	7949.16		1.8754		7.5995	
30	8172.61		1.8651		7.7366	
31	8390.57		1.8554		7.8768	
32	8603.05		1.8465		8.0201	
33	8810.05		1.8382		8.1666	
34	9011.59		1.8305		8.3165	
35	9207.69		1.8234		8.4697	
36	9398.38		1.8167		8.6265	
37	9583.66		1.8105		8.7870	
38	9763.57		1.8045		8.9512	

^a Not observed.

where

$$G(0) = \frac{Y_{10}}{2} - \frac{Y_{20}}{4} + \frac{Y_{30}}{8} + \frac{Y_{40}}{16} + \dots \quad (6)$$

and the value of Y_{00} is calculated from the expression

$$Y_{00} = \frac{Y_{01}}{4} + \frac{Y_{10}Y_{11}}{12Y_{01}} + \frac{(Y_{10}Y_{11})^2}{144(Y_{01})^3} - \frac{Y_{20}}{4}. \quad (7)$$

Using the spectroscopic constants from table 1 in the above expression, we get for the $A^1\Sigma^+$ state of KH

$$ZPE = 114.94 \text{ cm}^{-1}$$

$$G(0) = 113.10 \text{ cm}^{-1}$$

$$Y_{00} = 1.84 \text{ cm}^{-1}$$

$(G(v) + Y_{00})$ terms are built for $v = 0$ to 38 of the $A^1\Sigma^+$ state of KH molecule and RKR R_{\max} and R_{\min} are evaluated using the RKR1 program of Le Roy (1992). Table 2 shows these calculations. The RKR potential curve calculations of the $A^1\Sigma^+$ state of KH have been done by Almy and Beiler (1942), Jain and Sah (1963), Numrich and Truhlar (1975), Yang *et al* (1980) and Pardo *et al* (1987). However, we have compared our results given in table 2 with those of Yang *et al* (1980) recommended by Stwalley *et al* (1991). The values of ZPE , $G(0)$, Y_{00} of Yang *et al* (1980) are 115.17, 113.12 and 2.05 cm^{-1} , respectively, as compared to our respective values 114.94, 113.10 and 1.84 cm^{-1} . The uncertainty in ZPE is around 10 cm^{-1} due to the fact that levels for $v = 0, 1$ have not been observed for the $A^1\Sigma^+$ state. The ν_e value from Bartky's data (1966) is found to be 19060 cm^{-1} ; the value by Yang *et al* (1980) is given as $19057 \pm 25 \text{ cm}^{-1}$; that by Pardo *et al* (1987) is $19066 \pm 26 \text{ cm}^{-1}$ whereas from our calculations it is $19059 \pm 8 \text{ cm}^{-1}$. This large uncertainty is again attributed to the missing data of $v = 0, 1$ in the $A^1\Sigma^+$ state as already mentioned.

To conclude, the RKR potential has been constructed of the $A^1\Sigma^+$ state of KH from $v = 0$ to 38 based on the data of Bartky (1966) and Rafi *et al* (1993). The RKR calculations for $v = 27$ to 38 have been reported for the first time. The spectroscopic analysis of photoabsorption spectra of KH by Rafi *et al* (1993) provided the necessary data for this region of the $A^1\Sigma^+$ state.

We are grateful to Professor Le Roy, University of Waterloo, Ontario, Canada for providing the computer program for RKR calculations.

References

- Almy G M and Beiler A C 1942 *Phys. Rev.* **61** 476
 Almy G M and Hause C D 1932 *Phys. Rev.* **42** 242
 Bartky I R 1966 *J. Mol. Spectrosc.* **20** 299
 Hori T 1933 *Mem. Ryojun Coll. Eng.* **6** 1
 Hussein K, Effantin C, d'Incan J, Vergés J and Barrow R F 1986 *Chem. Phys. Lett.* **124** 105
 Jain D C and Sah P 1963 *J. Chem. Phys.* **38** 1553
 Klein O 1932 *Z. Phys.* **76** 221
 Le Roy R J 1992 *Chem. Phys. Res. Report* No CP-425, University of Waterloo
 Numrich R W and Truhlar D G 1975 *J. Phys. Chem.* **79** 2745
 Pardo A, Camacho J J, Poyato J M L and Martin E 1987 *Chem. Phys.* **117** 149
 Rafi M, Ali N, Ahmed K, Khan I A, Baig M A and Iqbal Z 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** L129
 Rees A L G 1947 *Proc. Phys. Soc. A*, **B** **59** 998
 Rydberg R 1931 *Z. Phys.* **73** 376; 1933 *Z. Phys.* **80** 514
 Stwalley W C, Zemke W T and Yang S C 1991 *J. Phys. Chem. Ref. Data* **20** 164
 Yang S C, Hsieh Y K, Verma K K and Stwalley W C 1980 *J. Mol. Spectrosc.* **83** 304