THE $X^1\Sigma^+$ GROUND STATE OF KH NEAR THE DISSOCIATION LIMIT

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Fluorescence excited in the $A^1\Sigma^+-X^1\Sigma^+$ system of ^{39}KH by the 4880 Å argon-ion laser line gives information about the ground state as far as the last bound rovibrational level. This is identified as $J = 6$ in $v = 23$, and, assuming a limit midway between $J = 6$ and $J = 7$, $D_e(KH) = 14776 \pm 4$ cm^{-1}.

1. Introduction

The $A^1\Sigma^+-X^1\Sigma^+$ systems of KH and KD have been the subject of a number of studies [1–8], beginning with the arc discharge emission work of Almy and Hause [1]. Recently, Giroud and Nedelec [9,10] have carried out time-resolved fluorescence studies of KH, using a microwave discharge, and have measured vibronic lifetimes in $A^1\Sigma^+$: they also observed vibrational and rotational energy transfer with H_2 and with plasma electrons. Theoretical investigations have included several pseudopotential calculations [11–14], a valence-bond calculation [15] and an FSGO SCF study [16]. There is, however, no currently available high-quality all-electron calculation on KH that is comparable to those for other hydrides [17–19]. Stwalley and co-workers have generated RKR potentials for KH [20] and for the other alkali hydrides [18,19,21–23]. More recently, Haese et al. [24] used infrared diode laser spectroscopy to determine precise information about the levels $0 \leqslant v \leqslant 2$ of the ground state.

In the present work, we report the results of the analysis of the fluorescence excited by the 4880 Å argon–ion laser which populates $v' = 7, J' = 6$ in $A^1\Sigma^+$. The fluorescence consists mainly of R(5), P(7) doublets, but some rotational satellites with $\Delta J' = \pm 1, \pm 2, \pm 3, ...$ were also observed. The spectrum was recorded at high resolution by Fourier transform spectrometry: it extends to $v'' = 23$, $J'' = 7$ at about 4 cm^{-1} above the dissociation limit.

2. Experimental

The fluorescence of KH was produced in a heat pipe containing potassium at 490°C with the pressure maintained at 7 mbar using argon as a buffer gas. No added hydrogen — other than that provided by impurities — was required.

3. Analysis and results

The fluorescence excited by Ar^+, 4880 Å was observed in two spectral regions: (i) in the visible region between 14345 and 20490 cm^{-1}, and assigned to $v'' = 0, 1, 2, 4, 5$ and 7, (ii) in the infrared between 6205 and 10285 cm^{-1}, assigned to $13 \leqslant v'' \leqslant 23$. The absence of intermediate doublets, with $8 \leqslant v'' \leqslant 12$, is explained by strong K_2 absorption in this region. Rotational relaxation was observed in the fluorescence to $v'' = 7, 16, 18, 20, 21, 22$ and 23 (fig. 1), but we have not been able ro record the lines due to vibrational relaxation reported by Pardo et al. [8].

Constants were determined in two stages. First, we made a simultaneous fit to all the lines of the seven vibrational levels for which we observed rotational relaxation plus the rotation—vibration lines published recently by Haese et al. [24]. Their precision is comparable with ours and their measurements provide valuable information about the levels $v = 0, 1$ and 2. The term values of the levels were represented by $T_{v,J} = T_v + B_v J(J + 1) - D_v J^2(J + 1)^2$.

In this way, ground-state constants G_v, B_v and D_v were determined for $v'' = 0, 1, 2, 7, 16, 18, 20, 21, 22$ and 23, and T_7, B_7 and D_7 for $A^1\Sigma^+$. Interpolation of the values of D_v'' then enabled values of G_v and of B_v to be determined for the levels for which only the principal P,R doublets were seen, namely, $v'' = 4, 5, 13, 14$ and 15. Values of the rotational constants derived in this way are given in table 1.

Dunham coefficients were derived from fits to the values of $\Delta G_{v+1/2}''$ and of B_v''. In the usual representation,

$$G(v, J = 0) = \sum_{i=0}^{n} Y_{i0}(v + \tfrac{1}{2})^i$$

whence

$$\Delta G_{v+1/2}(J = 0) = \sum_{k=0}^{n-1} H_k(v + \tfrac{1}{2})^k ,$$

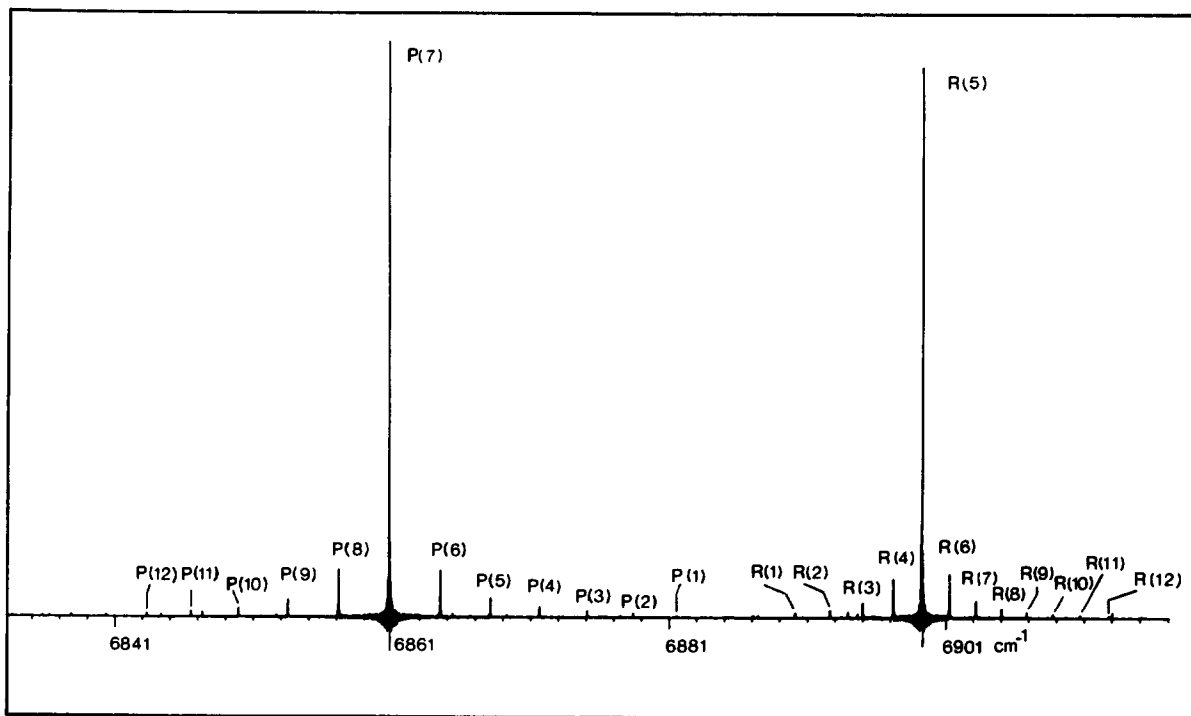where

$$H_k = \sum_{i=k+1}^{n} i!/k!(i - k)! .$$

Fig. 1. The 7—20 band of the $A^1\Sigma^+$–$X^1\Sigma^+$ system of KH.

Table 1
Values of B_v and D_v (cm^{-1})

v	B_v	$10^3 D_v$
0	3.37382(13)	0.1628(4)
1	3.28962(11)	0.1617(3)
2	3.20646(11)	0.1606(3)
4	3.04322 [a]	0.1588 [b]
5	2.96288 [a]	0.1577 [b]
7	2.80477(56)	0.1548(84)
13	2.32821 [a]	0.1550 [b]
14	2.24312 [a]	0.1602 [b]
15	2.15265 [a]	0.1682 [b]
16	2.05562(86)	0.1798(91)
18	1.82552(56)	0.2169(51)
20	1.50707(19)	0.3177(13)
21	1.28732(56)	0.4083(82)
22	1.00665(160)	0.6335(144)
23	0.67042	2.139

[a] Values of B_v derived from experimental values of $\Delta F''$ together with interpolated values of D_v.
[b] Interpolated values of D_v.

H_k is linear in the Dunham Y_{i0} coefficients and can therefore be determined by a least-squares fitting procedure. The value of Y_{00} is given by

$$Y_{00} = Y_{01}/4 - Y_{10}Y_{11}/12Y_{01} + (Y_{10}Y_{11})^2/144Y_{01}^3$$

$$+ Y_{20}/4 + \dots .$$

Values of the constants Y_{i0} and Y_{j1} are given in table 2. These values were used to determine the RKR po-

Table 3
RKR potential for the ground state, X $^1\Sigma^+$

v	G_v (cm^{-1})	r_{min} (Å)	r_{max} (Å)
		2.2401 [a]	
0	490.0779	2.0701	2.4458
1	1445.9460	1.9636	2.6226
2	2372.0117	1.8977	2.7599
3	3268.9001	1.8485	2.8823
4	4137.1550	1.8088	2.9969
5	4977.3077	1.7754	3.1070
6	5789.8479	1.7466	3.2143
7	6575.1859	1.7213	3.3203
8	7333.6301	1.6989	3.4258
9	8065.3740	1.6789	3.5317
10	8770.4781	1.6609	3.6384
11	9448.8363	1.6444	3.7467
12	10100.1221	1.6293	3.8572
13	10723.7138	1.6154	3.9710
14	11318.5972	1.6026	4.0894
15	11883.2384	1.5910	4.2141
16	12415.4080	1.5804	4.3476
17	12911.9331	1.5709	4.4936
18	13368.3517	1.5623	4.6580
19	13778.4686	1.5547	4.8508
20	14133.8621	1.5482	5.0903
21	14423.4918	1.5432	5.4138
22	14633.7253	1.5393	5.9144
23	14749.3488	1.5273	6.9828

[a] Value of r_e.

tential for the ground state of KH: values of the turning points are given in table 3, and the potential is illustrated in fig. 2.

Table 2
Molecular constants for the ground state, X $^1\Sigma^+$. The uncertainties quoted are values of 2σ. The number of figures retained are required to give a precision of 0.0001 cm^{-1} in calculated frequencies

|	G_v (cm^{-1})			B_v (cm^{-1})	
Y_{00}	0.670859	(0.22 E−03)	Y_{01}	3.4189506	(0.57 E−02)
Y_{10}	986.65055	(0.73 E−03)	$10Y_{11}$	−0.9439438	(1.66 E−02)
Y_{20}	−15.844615	(0.74 E−03)	$10Y_{21}$	0.106325415	(1.49 E−02)
Y_{30}	0.38533062	(0.36 E−03)	$10^2 Y_{31}$	−0.52310142	(0.62 E−03)
Y_{40}	−0.09217627	(1.01 E−04)	$10^2 Y_{41}$	0.14813303	(1.44 E−03)
Y_{50}	0.018413172	(1.74 E−05)	$10^3 Y_{51}$	−0.248376412	(0.20 E−04)
$10^2 Y_{60}$	−0.2385268	(1.96 E−06)	$10^4 Y_{61}$	0.25605538	(1.78 E−05)
$10^3 Y_{70}$	0.20131181	(1.44 E−07)	$10^5 Y_{71}$	0.633047058	(0.64 E−07)
$10^4 Y_{80}$	−0.11081649	(0.70 E−08)	$10^7 Y_{81}$	−0.163822469	(1.00 E−06)
$10^6 Y_{90}$	0.38314085	(0.21 E−09)	$10^8 Y_{91}$	0.13521347	(0.34 E−07)
$10^8 Y_{10,0}$	−0.75651294	(0.36 E−11)	$10^{10} Y_{10,1}$	0.1223840112	(0.54 E−11)
$10^{10} Y_{11,0}$	0.64835269	(0.28 E−13)			
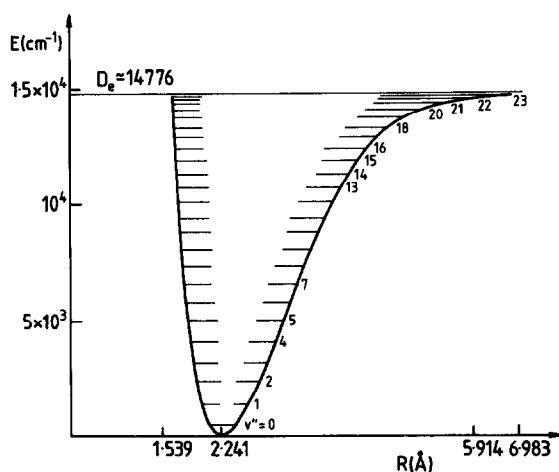
Fig. 2. RKR potential energy curve for the X state of KH.

4. The dissociation limit of the ground state of KH

The results given above have provided a precise experimental description of the rotationless potential for the ground state as far as $v = 23$. It should be noted that the last observed levels in this state correspond to values of r_{max} which are too short for the application of LeRoy—Bernstein long-range theory, the usual criterion for whose applicability is, for $K(4s\,^2S) + H(1s\,^2H)$, $r > 7.3$ Å [25], whereas the

value of r_{max} for the highest observed level, $v = 23$ (at 99.8% of D_e), is 6.98 Å. Moreover, the rapid change of the molecular constants linked with the partial ionic character of this state makes very uncertain attempts at the determination of the dissociation limit by classical methods of extrapolation. By good fortune, the detailed observation of the spectrum in the region of the 7–23 band enables us to derive a precise value of the dissociation limit.

As can be seen in fig. 3, the lines R(5), R(6) and P(6) of the 7–23 band are observed with a width (fwhm) of about 0.04 cm^{-1}, which approximates to the instrumental width. However P(7) is considerably broader ($\approx$0.4 cm^{-1}). The identification of the main lines R(5) and P(7) is confirmed by the observation of the relaxation lines R(6) and P(6), whose separation, 36.785 cm^{-1}, is identical within the experimental error, to the mean of the R(6)–P(6) separations in the 7–7, 7–16, 7–18, 7–20, 7–21 and 7–22 bands, namely 36.788 cm^{-1}.

These observations indicate that the dissociation limit of the ground state lies between $J = 6$ and 7 in $v'' = 23$. The energies of these levels with respect to the minimum in X$^1\Sigma^+$ are 14773.73 and 14780.18 cm^{-1}, respectively. D_e is then 14777 ± 4 cm^{-1}. This value can be compared with the theoretical estimate of 14490 cm^{-1} proposed by Stevens et al. [11] and with a previous experimental value, 15020 ± 400 cm^{-1} obtained by Yang et al. [26].
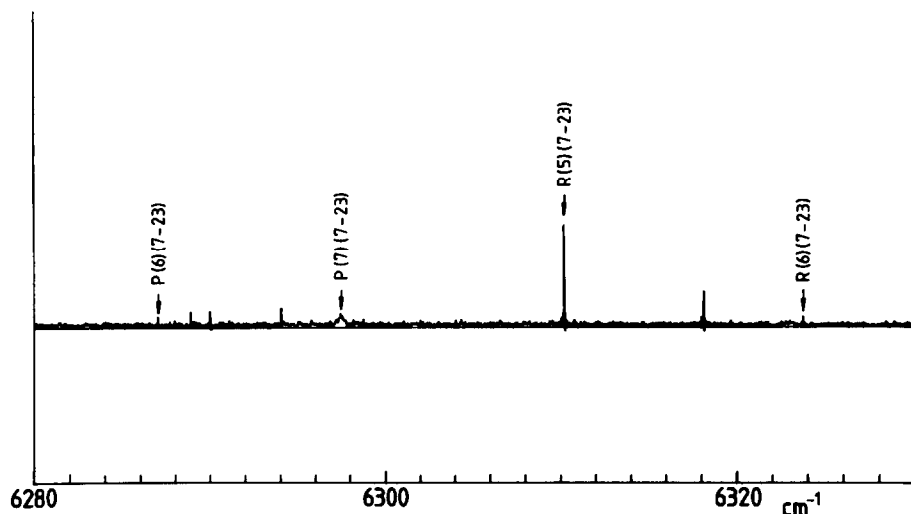

Fig. 3. The 7–23 band of the A$^1\Sigma^+$–X$^1\Sigma^+$ system.

Acknowledgement

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