

## NEW SELF-CONSISTENT POTENTIALS FOR THE $X'^1\Sigma^+$ AND $A'^1\Sigma^+$ STATES OF KH.

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### ABSTRACT

The vibrational and rotational molecular constants have been determined for the  $A'^1\Sigma^+ - X'^1\Sigma^+$  system of the isotopic potassium hydrides: KH and KD. From these experimental term values, isotopically combined PMO-RKR-van der Waals potentials are constructed, which are checked by direct integration of radial Schrödinger equation. As an additional check on the accuracy of the potentials, the wavefunctions were used to compute  $B_v$ ,  $D_v$ ,  $H_v$  and  $L_v$  values. The agreement between the calculated and experimental results is quite satisfactory. Franck-Condon overlap integrals and probability density distributions have been calculated. The anomalous behaviour of the  $A'^1\Sigma^+$  state may be observed in the probability density functions of the lowest vibrational levels.

### INTRODUCTION

This paper on KH is part of a larger study on the spectroscopy and structure of the  $X'^1\Sigma^+$  and  $A'^1\Sigma^+$  states of the alkali metal hydrides (Refs. 1-4).

The KH  $A'^1\Sigma^+ - X'^1\Sigma^+$  electronic spectrum has been subject of a number of studies (Refs. 5-8). In our laboratory we have also studied the fluorescence spectrum by the  $Ar^+$  4881 Å exciting line. This produces only the excitation transition ( $v''=0$ ,  $J''=5 \rightarrow v' = 7$ ,  $J' = 6$ ), although important populations of vibro-rotational states adjacent to the excited state are induced by collisions (Refs. 2-3).

In this work we report for  $X'^1\Sigma^+$  and  $A'^1\Sigma^+$  states of KH a revised set of isotopically combined spectroscopic constants. From these spectroscopic term values for both ground and excited

states have been generated. Exact vibrational eigenfunctions were obtained by direct numerical solution of the radial Schrödinger equation. As an additional check on the accuracy of the potentials, the wavefunctions were used to compute the rotational constants  $B_v$  and the centrifugal distortion terms  $D_v$ ,  $H_v$  and  $L_v$ . From the wavefunctions we calculated the probability density distributions and the Franck-Condon factors for the  $A'\Sigma^+ \leftrightarrow X'\Sigma^+$  band system of KH. It has been found that the probability distribution functions for the  $A'\Sigma^+$  state show a reversed asymmetry, explaining the anomalous behavior of that state.

#### MOLECULAR CONSTANTS

Using programmes developed in our laboratory we have determined the isotopically combined molecular constants from least-squares fit to the expressions:

$$\nu^i(v', v'') = T_e + \sum_{i=1} Y'_{i0} (\eta')^i - \sum_{i=1} Y''_{i0} (\eta'')^i \quad (1)$$

$$B_v \rho^2 = \sum_{i=0} Y_{i1} \eta^i \quad (2)$$

where  $\eta = (v + 1/2)/\rho$  and  $\nu^i(v', v'') = \nu(v', v'')/\rho$  with  $\rho = 1$  for KD and  $\rho = 0.71624443$  for KH.

TABLE 1.- Vibrational and rotational spectroscopic constants ( $\text{cm}^{-1}$ ) for the  $X'\Sigma^+$  and  $A'\Sigma^+$  states of KH.

$j, k$	$Y'_{jk}$ (X State)	Stan. Dev.	$Y''_{jk}$ (A State)	Stan. Dev.
			$T_e = 19066.0$	3.49
1,0	987.4906992	0.49	220.1726585	1.8
2,0	-16.13270476	0.25	7.640342154	0.34
3,0	0.3326896132	4.9E-2	-0.3529548606	2.8E-2
4,0	-2.95880988E-2	4.3E-3	7.17800082E-3	1.0E-4
5,0	1.63391556E-3	1.8E-4	-7.11651189E-5	1.5E-6
6,0	-3.88995176E-5	2.6E-6		
0,1	3.42608456	7.7E-3	1.20972138	3.4E-2
1,1	-9.51553364E-2	7.6E-3	6.84896154E-2	1.4E-3
2,1	4.79238162E-3	2.2E-4	-7.16611436E-3	1.7E-4
3,1	-7.08484904E-4	2.5E-5	2.72590467E-4	8.9E-6
4,1	4.75740295E-5	1.6E-6	-4.01796024E-6	1.5E-7
5,1	-1.18329205E-6	2.2E-7		

For these calculations we have used data of the laser-induced fluorescence spectrum photographed in our laboratory (Ref. 2) as well as the previous data (Ref. 5-8). Table 1 shows isotopically combined spectroscopic molecular constants obtained by us.

#### POTENTIALS ENERGY CURVES

The hybrid potential energy curves for the X and A states (fig. 1 and table 2) are constructed throughout the well in a fashion similar to that for the ground and excited states of LiH (Ref. 1). The full potential consists of a seventh-order lagrangian interpolation of the RKR points (including higher-order effects in WKB approximation) plus a perturbed Morse potential for the minimum zone and a long-range potential for the asymptotic zone.

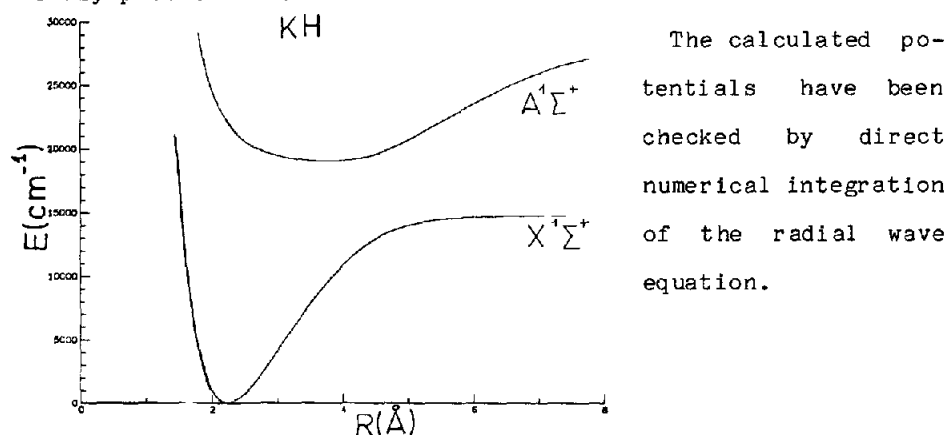


Fig. 1. Potentials energy curves for  $X(\Sigma^+)$  and  $A(\Sigma^+)$  states of KH.

As an additional check on the accuracy of the potentials, the wavefunctions were used to compute the rotational constants and the centrifugal distortion terms, following the Albritton treatment (Ref. 9). Table III compares the experimental results for  $B_v$ ,  $D_v$ ,  $H_v$  and  $L_v$  with those calculated.

TABLE 2.- Experimental terms and eigenvalues ( $\text{cm}^{-1}$ ) for the RKR region of the potentials for the X and A states of KH.

v	$A'\Sigma^+$ state		$X'\Sigma^+$ state	
	$G(v)+Y_{00}$	Eigenvalue	$G(v)+Y_{00}$	Eigenvalue
0	490.45	490.36	114.00	114.06
2	2372.79	2372.61	594.99	595.40
5	4979.31	4979.86	1391.60	1391.86
8	7336.47	7336.76	2243.08	2243.46
11	9450.43	9449.95	3118.90	3119.22
14	11319.47	11318.04	3996.59	3996.64
17	12913.57	12912.40	4859.72	4859.60
20	14133.56	14132.60	5695.74	5695.96
23	14749.93	14754.09	6493.98	6495.05
26			7243.53	7244.72

TABLE 3.- Calculated and experimental values for the rotational constants ( $\text{cm}^{-1}$ ) for the  $A'\Sigma^+$  and  $X'\Sigma^+$  states of KH.

Ground state							
v	$B_v(\text{Cal.})$	$B_v(\text{Exp.})$	$D_v(\text{Cal.})$ $\times 10^4$	$D_v(\text{Exp.})$ $\times 10^4$	$H_v(\text{Cal.})$ $\times 10^4$	$H_v(\text{Exp.})$ $\times 10^4$	$L_v(\text{Cal.})$ $\times 10^{13}$
0	3.379771	3.379619	1.6383	1.6284(a)	5.988	7.68(b)	-3.63
1	3.292111	3.291975	1.6202	1.6173	6.659	-	-4.72
2	3.208326	3.208821	1.6056	1.6063	6.729	-	-
3	3.126593	3.127889	1.5887	-	-	-	-
4	3.045110	3.047695	1.5718	1.5880	-	-	-
5	2.963299	2.967403	1.5508	1.5770	-	-	-
6	2.881829	2.886678	1.5284	-	-	-	-
7	2.801259	2.805546	1.5092	1.5488	-	-	-
8	2.719742	2.724252	1.4949	-	-	-	-
9	2.639471	2.643117	1.4845	-	-	-	-
Excited state							
0	1.241570	1.242208	1.4423	1.2078	55.06	-	-233.9
1	1.295078	1.297232	1.4135	1.1818	41.05	-	-119.6
2	1.338006	1.340259	1.3937	1.1559	31.07	-	-
3	1.371818	1.372735	1.3543	1.1299	18.81	-	-
4	1.394883	1.396003	1.3060	1.1039	14.29	-	-
5	1.410144	1.411315	1.2693	1.0779	10.78	-	-
6	1.419508	1.419823	1.2141	1.0519	-	-	-
7	1.421927	1.422586	1.1597	1.0259	-	-	-
8	1.420129	1.420562	1.1188	0.9999	-	-	-
9	1.414798	1.414617	1.0698	0.9739	-	-	-

(a) Ref. 8; (b) Ref. 7; (c) Ref.5

## FRANCK-CONDON OVERLAP INTEGRALS AND PROBABILITY DENSITY FUNCTIONS

To explain the intensity distribution in absorption, the squares of the overlap integrals of the  $v''=0$  progression are

schematically shown in fig. 2(a). In fig. 2(b), we also plot the Franck-Condon factors (FCF) for band progressions in emission having  $v'=7$  (laser transition).

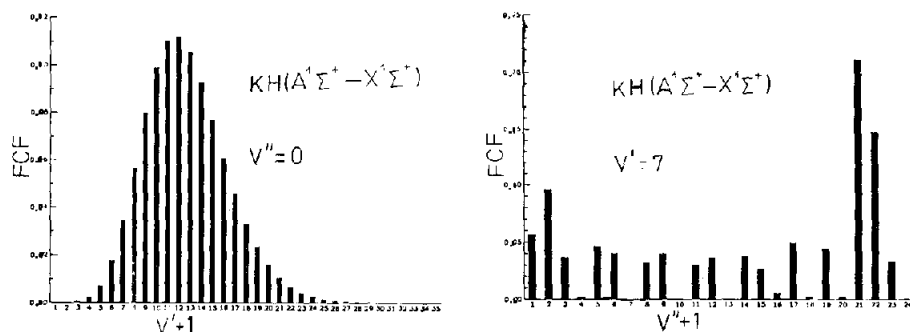


Fig.2.- FCF for: (a)  $v''=0$  progression and (b)  $v'=7$  progression.

It can be seen that there are two intensity maxima present in the emission progression for  $v''=20$  and  $v''=21$ .

In Fig. 3 we show the FCF for the experimental observed vibrational bands. The vibrational levels with  $v'=8$ , 6 and 5 are due to vibrational relaxation induced by collision mechanisms. It is observed a qualitative agreement between these values with the experimental observation.

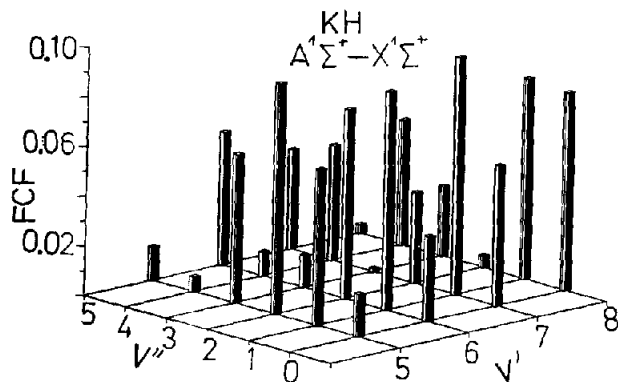


Fig.3.- FCF for the experimental observed vibrational bands.

Interesting anomalies and perturbations appear in the spectra of alkali hydrides. We have observed that the anomalous

behaviour of the  $A'\Sigma^+$  state is clearly shown in the probability density distributions of the lowest vibrational levels. In fig. 4 we show the probability density functions for the  $A'\Sigma^+$  and  $X'\Sigma^+$  states with  $v=1$  and 2.

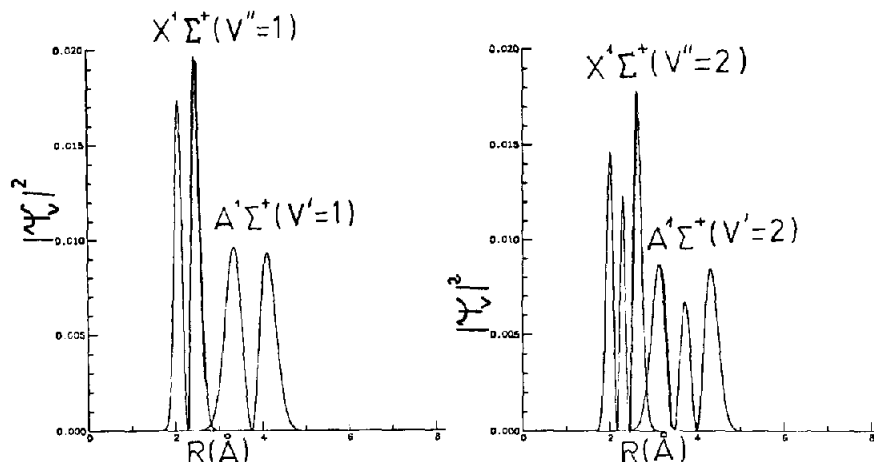


Fig.4 .-Probability density distributions for  $A'\Sigma^+$  and  $X'\Sigma^+$  states: (a)  $v'=v''=1$  ; (b)  $v'=v''=2$ .

It is observed that in the  $A'\Sigma^+$  state (for  $v'=1-4$ ) is more probable to find the molecular system in positions near the minimum turning points than near the maximum turning points.

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