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Potential Energy Curve of the Excited State of KH

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The $^1\Sigma \rightarrow {}^1\Sigma$ spectrum of KH has been photographed at large dispersion and the region from 4150A to 4650A has been analyzed. Previous analyses of the spectrum have on the whole been verified, although certain discrepancies in molecular constants have been removed. For the purpose of testing Mulliken's explanation of the anomalous character of the excited state of an alkali hydride, a potential curve has been constructed for the excited state of KH, by the use of Klein's method. The vibrational energy of the upper state of KH has been followed to about three-fourths of the energy of dissociation, farther than in any other alkali hydride. As in LiH, the curve of the excited state crosses the ionic curve (of K^+ and H^-) and dissociates apparently into $K(^2P)$ and $H(^2S)$. The relative position of the molecular and ionic curves is in reasonable agreement with Mulliken's hypothesis.

INTRODUCTION

THE excited $^1\Sigma$ state of each of the alkali hydrides exhibits an anomalous behavior which appears in the unusual values of the vibrational and rotational constants. The vibrational frequency at small amplitude (ω_e) is surprisingly small for this type of molecule and the vibrational intervals increase to a maximum with increasing amplitude of vibration, instead of decreasing monotonically as in all other known diatomic states. The rotational constant B_v follows a roughly parallel course with increasing v. These unusual constants derive from an anomalous potential energy curve, which is unusually flat at the bottom, rises more steeply than the parabola which fits near r_e, and has less asymmetry than diatomic potential energy curves usually do.

Mulliken[1] has discussed and compared the constants of the alkali hydrides and has proposed that the unusual shape of the upper state potential curve can be understood by assuming that the two low states of an alkali hydride arise from the interaction between two $^1\Sigma^+$ states, one homopolar and derived from unexcited neutral atoms, the other ionic and derived from M^+ and H^-; where M is an alkali atom. Since, however, the excited state dissociates not into the ions, but, in all probability, into M (^2P) and H (^2S), it is also necessary to assume a second similar interaction, between the $^1\Sigma^+$ state derived from M (^2P) and H (^2S) and the $^1\Sigma^+$ state of M^+ and H^-.

The first test of the theory consists in constructing a good potential curve for the upper state of an alkali hydride and comparing its course at $r > r_e$ with that of the nearly coulomb curve of the ionic state. If the second interaction, near dissociation, is neglected the potential curve should go smoothly into the ion-pair curve. Because of the rapid change in vibrational and rotational constants for low v, good values of the equilibrium constants cannot be obtained. Hence the usual empirical methods of choosing parameters in an equation for the potential in such a way that the potential curve will then reproduce the observed vibrational and rotational constants are not trustworthy, especially for the higher vibrational energies.

It is necessary to use a method, such as Rydberg's, in which the curve is built up step by step, so shaped, as the potential energy increases, that (1) the action integral for the linear momentum equals $(v+\frac{1}{2})h$ for the observed energy levels, and (2) the mean value of $1/r^2$ for each vibrational state corresponds to the observed $1/r^2$ obtained from B_v. A convenient method of constructing a curve which satisfies these conditions has been given by O. Klein.[2] It has been applied to LiH by Rosenbaum[3] who made use of the excellent data of Crawford and Jorgensen.[4]

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[1] R. S. Mulliken, Phys. Rev. **50**, 1028 (1936).

[2] O. Klein, Zeits f. Physik **76**, 226 (1932).

[3] E. J. Rosenbaum, J. Chem. Phys. **6**, 16 (1938).

[4] F. H. Crawford and T. Jorgensen, Phys. Rev. **47**, 932 (1935).

The results on the whole supported Mulliken's theory.

In the case of CsH a good potential curve has not been constructed, but it has been shown[5] by means of a power series curve that the upper state has about the predicted relation to the ionic curve.

The spectrum of KH has been analyzed by Almy and Hause,[6] using low dispersion, and by Hori.[7] Hori extended the upper state to $v'=24$, a vibrational energy of 0.84 ev, about three-fourths of the energy of dissociation. The corresponding state in LiH has been followed only about halfway to dissociation. Since the course of the potential curve near dissociation is of special interest in connection with Mulliken's hypothesis it seemed desirable to construct a potential curve for the excited state of KH and to compare it with the ionic curve. That is the principal object of this paper. Certain discrepancies in molecular constants are also discussed and a list of the most likely values of the constants and the energies of dissociation of both states of KH is included.

NEW MEASUREMENTS OF THE SPECTRUM OF KH

Hori obtained the spectrum with an arc source and a spectrograph of medium dispersion (three-meter grating). There were a great many blends of lines, observed lines being assigned frequently to several bands. Since the spectrum is of the many lines type (no band edges) a rotational analysis and location of band origins must precede a vibrational analysis. In bands of high v', however, lines for $K<10$ were apparently not observed by Hori. Lines of low K are best for determining the origin. For these reasons it seemed worthwhile to rephotograph the spectrum and to check the analysis in the region of large v'. It turned out that no important changes were made in values of vibrational energy.

The spectrum was excited in a tube of the design used by Gaydon and Pearse[8] for tne excitation of RbH. This is a much better method than the arc in hydrogen. In our arrangement a tube 3.5 cm by 75 cm carried a waxed-on window at one end, a removable ground joint plug at the other and four side tubes, two for electrodes, two for passing through hydrogen. In the center of the tube was mounted a quartz tube 1 cm by 10 cm, carried in a steel cradle the ends of which were disks fitting loosely into the glass tube and drilled to admit the quartz tube. With a large positive column the potential drop through the quartz tube becomes less than the cathode fall to the steel cradle and an intense constricted discharge runs through the quartz tube. A potential of 3000 volts was supplied from a 5-kva transformer and a current density of 0.12 to 0.19 ampere per sq. cm was obtained in the constriction when tank hydrogen at 3- to 5-mm pressure was flowed through the tube. A little potassium was placed in a bulge on the quartz tube. Refilling was necessary only after several hours of operation.

The KH spectrum was strongly excited and was photographed from 4000A to 6000A in the first order of a 21-foot grating at a dispersion of about 1.3A per mm. The iron arc was photographed for wave-length standards. A spectrum of a hydrogen discharge without potassium, at about the same pressure, was also photographed to enable one to identify the H_2 lines. Only the strongest of these appeared in the KH discharge spectrum. They were also distinguished by being relatively much more diffuse than KH lines.

The positions of about 1200 lines on the best exposure were measured twice, independently, and their wave-lengths computed relative to iron International Secondary Standards. Wave numbers in vacuum were obtained from Kayser's tables. The measurements were made only in the range from 21,634 cm^{-1} to 23,968 cm^{-1}, the latter being near the highest wave number observed in the spectrum of KH. This range covers bands with v' between 9 and 24. The table of wave numbers is too extensive to be included here.

ANALYSIS OF BANDS

In making the analysis, branches were picked out by the criterion of constant second differences along a branch and followed in nearly every case to $K=0$ or 1. Each band analyzed had one vibrational state in common with at least one other band. Combination differences (Δ_2F) were

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[5] G. M. Almy and M. Rassweiler, Phys. Rev. **53**, 890 (1938).

[6] G. M. Almy and C. D. Hause, Phys. Rev. **42**, 242 (1932).

[7] T. Hori, Mem. Ryojun Coll. Eng. **6**, 1 (1933).

[8] A. G. Gaydon and R. W. B. Pearse, Proc. Roy. Soc. **173**, 28 (1939).

TABLE I. Origins and constants of bands reanalyzed. Values by Hori in parentheses.

B_v'	$D_v' \times 10^5$	B_v'' $D_v'' \times 10^5$	(3.3730) (15.5)	(3.2960) (15.9)	(3.2154) (16.0)	(3.127) (15.8)	
		v' v''	0	1	2	3	$\Delta G'(v'+\frac{1}{2})$
1.394 (1.3934)	(9.4)	9	21,692.42 (21,692.4)				
							293.19 (293.3)
1.383 (1.3814)	(9.3)	10	21,985.61 (21,985.7)				
							292.83 (292.8)
1.370 (1.3679)	(9.2)	11	22,278.44 (22,278.5)				
							291.57 (291.1)
1.354 (1.3528)	12.2 (9.0)	12	22,570.01 (22,569.6)				
							289.91 (289.8)
1.337 (1.3366)	(8.9)	13	22,859.92 (22,859.4)				
							287.63 (287.6)
1.319 (1.3188)	(8.7)	14	23,147.55 (23,147.0)	(22,192.5)			
							285.06 (285.7)
1.299 (1.2984)	8.9 (8.5)	15	23,432.61 (23,432.7)	(22,478.2)			
							281.98 (282.4)
1.278 (1.2776)	8.3 (8.3)	16	23,714.59 (23,715.1)	(22,760.6)			
							278.51 (278.6)
1.263 (1.2565)	9.6 (8.1)	17	23,993.10 (23,993.7)	23,037.48 (23,039.2)			
							274.74 (274.8)
1.239 (1.2353)	8.6 (7.8)	18	(24,268.5)	23,312.23 (23,314.0)	(22,388.3)		
							270.69 (271.6)
1.212 (1.2105)	6.7 (7.6)	19	(24,540.1)	23,582.92 (23,585.6)	(22,659.9)		
							266.04 (267.2)
1.190 (1.1854)	19.5 (7.4)	20	(24,807.3)	23,848.96 (23,852.8)	22,922.93 (22,927.1)		
							261.07 (261.7)
1.180 (1.1600)	10.59 (7.1)	21	(25,069.0)	(24,114.5)	23,184.00 (23,188.5)		
							256.19 (253.8)
1.142 (1.1342)	8.0 (6.9)	22		(24,368.3)	23,440.19 (23,442.6)		
							249.94 (250.8)
1.124 (1.1102)	10.2 (6.7)	23		(24,619.1)	23,690.13 (23,693.4)		
							244.6 (241.9)
1.082 (1.0852)	7.0 (6.5)	24		(24,861.0)	23,934.7 (?) (23,935.3)	23,034.9 (?) (23,035.4)	
	$\Delta G''(v''+\frac{1}{2})$		955.61 (954.5)	926.21 (925.7)	899.6 (899.0)		

computed for all bands analyzed and where these differences were common to two bands, they were found to be equal within errors of measurement.

The rotational constants and band origins were computed by graphical methods. The band origins, rotational constants and vibrational intervals (ΔG) are listed in Table I. Values in parentheses are given by Hori.

For the excited state good values of the vibrational and rotational equilibrium constants are difficult to obtain because of the rapid anomalous changes of $\Delta G'$ and B'_v for v' near zero. Almy and Hause, fitting the values of $\Delta G'$ to a power series in $v'+\frac{1}{2}$ by least squares, with v' running from 0 to 16, found $\omega'_e = 254.5$ cm^{-1}, $x'_e\omega'_e = -3.26$ cm^{-1}. Hori gives an expression which represents the band origins in which $\omega'_e = 240.18$, $x'_e\omega'_e = -7.015$, values which are certainly in error. Crawford and Jorgensen[4] have shown that the constants obtained by least squares in the similar situation in LiH depend markedly on the number of vibrational levels used.

In view of these discrepancies it appears that the most trustworthy procedure for getting ω'_e and $x'_e\omega'_e$ is a plausible extrapolation of a plot of $\Delta G' = G'(v'+1) - G'(v')$ against $(v'+1)$ to ω'_e, the intercept at $v'+1=0$. Such a plot (data from reference 6), Fig. 1, shows that $\omega_e < 254.5$ and that it is 251.0 with an uncertainty of about 1 cm^{-1}. From the slope at the intercept $x_e\omega_e$ is estimated to be -4.5.

A reconsideration of B'_v by similar graphical methods and use of the data of Hori, and Almy and Hause, for bands of low v', leads to an estimate of $B'_e = 1.32 \pm 0.01$ in agreement with Hori's 1.311. α'_e is estimated to be -0.04; Hori gives -0.0527.

TABLE II. Summary of constants of the band spectrum of potassium hydride.

	Ground state	Excited state
T_e (cm^{-1})	0	19,530.2
ω_e (cm^{-1})	985.0	251.0
$x_e\omega_e$ (cm^{-1})	14.65	-4.5
B_e (cm^{-1})	3.415	1.32 ± 0.01
α_e (cm^{-1})	0.083	-0.04
r_e (10^{-8} cm)	2.24	3.60
I_e (10^{-40} g cm^2)	8.20	21.2
a_0 (cm^{-1})	17,027.0	11,932.0
a_1	-2.168	-0.04
a_2	3.015	2.275
D_e (ev)	1.92	1.10 ± 0.15

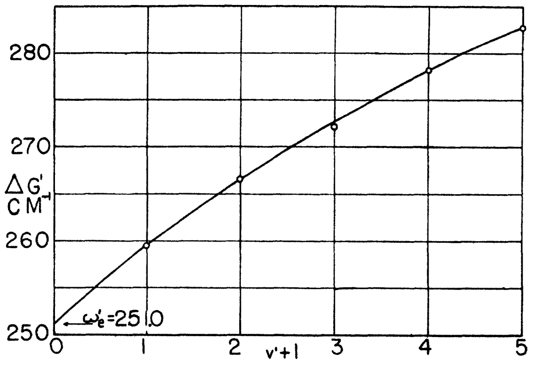

FIG. 1. Large scale plot of $\Delta G'$ *vs.* $v'+1$ at small v' to show intercept, ω_e.

The constants of the ground state of KH are not anomalous. From a consideration of previous and present work the best available values of the constants of the two states are believed to be those included in Table II.

POTENTIAL ENERGY CURVE OF THE EXCITED STATE

For internuclear distances very close to r_e the potential energy curve may be represented by the usual power series.

$$U(r) = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + \cdots),$$

where

$$a_0 = \omega_e^2/4B_e, \quad a_1 = -(1 + \alpha_e\omega_e/6B_e^2),$$
$$a_2 = 5/4a_1^2 - 2x_e\omega_e/3B_e, \quad \xi = (r - r_e)/r_e.$$

The calculated values of the coefficients are given in Table II and $U(r)$ near r_e is plotted in Fig. 2.

Except near r_e Klein's method of constructing a potential energy curve has been used. This method is based on a classical point of view and cannot be used for the lowest values of v. Klein develops a function,

$$S(V, \kappa) = \frac{1}{\pi(2\mu)^{\frac{1}{2}}} \int_0^{I'} [V(r) - E(I, \kappa)]^{\frac{1}{2}} dI,$$

in which $\kappa = P^2/2\mu$, where P is the angular momentum and μ is the reduced mass of the molecule; $V(r)$ is the effective potential energy, $U(r) + \kappa/r^2$; I is the radial action variable, $\oint p_r d_r$; and E is the total energy in excess of energy at r_e. I' is the value of I for which $V(r) - E(I, \kappa) = 0$. He shows that from partial

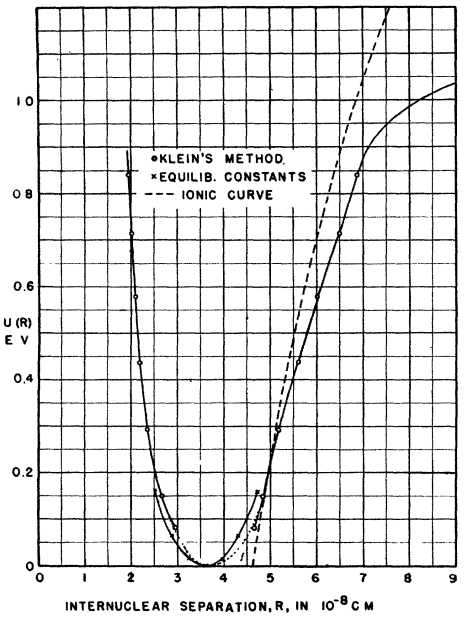

FIG. 2. Results of potential energy calculations.

derivatives of S one can compute $r_{\min}$ and $r_{\max}$ of the potential curve for any selected value of V. Thus, if $f=\partial S/\partial V$ and $g=-(\partial S)/(\partial\kappa)_{\kappa=0}$, then $r_{\max}=(f/g+f^2)^{\frac{1}{2}}+f$, $r_{\min}=(f/g+f^2)^{\frac{1}{2}}-f$. In applying the method to the quantized motion of a molecule one replaces I by $(v+\frac{1}{2})h$ and κ by $(h^2/8\pi^2)K(K+1)$.

The steps followed in obtaining f are as follows. The term values G_v of the vibrational energy states are tabulated, referred to the bottom of the potential curve as zero. One then selects, as a value of $V(r)$, a particular term G_i and subtracts from it each G_v for which $v<i$. Then $(G_i-G_v)^{\frac{1}{2}}$ is plotted against $v+\frac{1}{2}$ and the area under the curve is measured from $v+\frac{1}{2}=0$ to $v+\frac{1}{2}=i+\frac{1}{2}$ (at which point $G_i-G_v=0$, or $V(r)-E(I,\kappa)=0$). The area thus obtained when multiplied by the proper constant is a graphical integration giving a value of Klein's function S. S was thus computed for seven values of V. S was plotted against V and f was found graphically for several values of $V=G_v$, from the slope of the curve.

To obtain g, it is necessary to find the rate of change of S with rotation, or K, at the values of G_v or V for which f was calculated. To this end quantities of the form

$$\{G_i-[G_v+B_vK(K+1)]\}$$

must be plotted against $v+\frac{1}{2}$ and integrated graphically to get $S(I,\kappa)$ for various values of κ, and the derivatives $\partial S/\partial\kappa=-g$ calculated. Since, for small K, $BK(K+1)$ is much less than G_i-G_v the difference

$$\theta_{i,K}=(G_i-G_v)^{\frac{1}{2}}-\{G_i-[G_v+B_vK(K+1)]\}^{\frac{1}{2}}$$

may be expanded as a power series in $B_vK(K+1)/(G_i-G_v)$. $\theta_{i,K}$ was calculated by means of this series, plotted against $(v+\frac{1}{2})$ for $K=2$ and $K=4$ and integrated to get the change in S with K and hence with κ. In making this plot, special care has to be taken in the energy interval nearest G_i, as G_v approaches G_i. The rate of change of S with κ is nearly constant for small κ.

Table III and Fig. 2 contain the results of the potential energy curve calculation by the method described.

ENERGIES OF DISSOCIATION AND RELATION OF POTENTIAL CURVES TO IONIC CURVE

To fix the relative position of the ionic curve and the upper state curve, and thereby to test Mulliken's hypothesis, it is necessary to determine from the spectroscopic data the energy of dissociation of either the upper or lower state.

In the lower state the vibrational intervals decrease linearly in the short range observed, $v''=0$ to $v''=4$. From the constants (Table II), $D''_e=\omega''^2_e/4x_e\omega_e=16{,}560$ cm^{-1} $=2.05$ ev. This method usually gives too high a value of D_e.

Figure 3 shows a plot of $\Delta G'$ against $v'+1$. The area under the curve, when extrapolated to $\Delta G'=0$, is D'_e. A linear extrapolation gives $D'_e=1.43$ ev. This is probably too high but certainly shows that the upper state does not dissociate into K$^+$ and H$^-$. For, in this case, $D'_e=D''_e+$(I.P. of K)$-$(electron affinity of H)$-\nu_e=3.2$ ev. Thus the most likely products of

TABLE III. Calculation of potential curve by Klein's method.

v'	$U(r)$ ev	g 10^8 cm^{-1}	f 10^{-8} cm	$r_{\min}$ A	$r_{\max}$ A
2	0.0810	0.0615	0.849	2.962	4.660
4	0.1492	0.0842	1.086	2.666	4.838
8	0.2923	0.1156	1.410	2.346	5.176
12	0.4375	0.1389	1.712	2.194	5.618
16	0.5794	0.1544	1.959	2.106	6.024
20	0.7146	0.1707	2.242	2.019	6.503
24	0.8399	0.1829	2.462	1.956	6.880

dissociation for the excited state are K (^2P) and H (^2S). Combining this assumption with $D''_e = 2.05$ ev, one finds $D'_e = D''_e + \mathrm{K}\ (^2P) - \nu_e = 2.05 + 1.60 - 2.42 = 1.23$ ev, which is 0.2 ev less than obtained by linear extrapolation of the upper state. Since 2.05 ev is an upper limit for D''_e, 1.23 ev is an upper limit for D'_e.

A lower limit of D'_e can also be set. The bands were followed to $v' = 24$, vibrational energy 0.84 ev. This lower limit can be raised somewhat since there is no evidence of rotational dissociation. The bands with $v' = 24$ were weak and not well developed but the band (23, 2) was followed to $K = 30$, which corresponds to a rotational energy of 0.130 ev, or vibrational plus rotational energy of 0.940 ev. Of course a molecule may possess vibrational plus rotational energy in excess of its heat of dissociation since there is a maximum in the effective potential curve when $K > 0$, due to the centrifugal potential $(B_e r_e^2/r^2 K(K+1))$, which is 0.152 ev at $r_e = 3.6$A, and 0.041 ev at $r = 6.9$A, the greatest r reached in the accurate potential curve. Since the curve is rising steeply at this point the maximum must occur at larger r and it is safe to conclude that the centrifugal potential is not more than 0.02 ev at the maximum of the curve for $K = 30$. Thus a lower limit on D'_e is placed at $0.94 - 0.02$ or 0.92 ev. In this argument it is assumed that the potential curve for $K = 0$ has no maximum.

Thus D'_e is placed between limits of 0.92 ev and 1.23 ev. One can conclude that D'_e is 1.10 ev with an uncertainty of 0.15 ev. From this it follows that $D''_e = \nu_e + D'_e - \mathrm{K}\ (^2P) = 2.42 + 1.10 - 1.60 = 1.92$ ev.

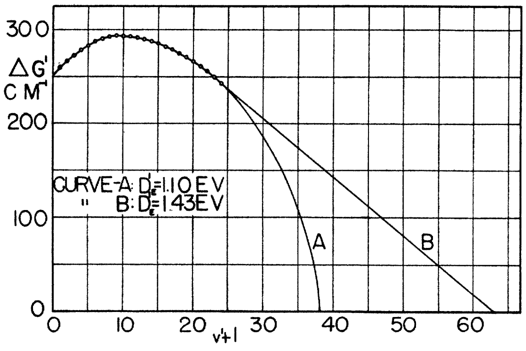

FIG. 3. Plot of $\Delta G'$ against $v'+1$. Area under curve is D'_e, the heat of dissociation of the excited state. Curve B is a linear extrapolation of the plotted data. Curve A is based upon a better method (see text) of estimating D'_e.

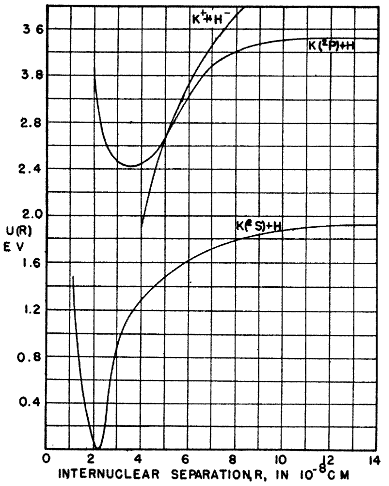

FIG. 4. Potential energy curves of KH molecule.

With D'_e and D''_e fixed the curve for $\mathrm{K}^+ + \mathrm{H}^-$ at large r can be drawn as in Fig. 4. Referred to K (^2S)+H (^2S) as zero energy, its equation is $U(r) = 3.60 - (14.4/r)$, in electron volts, r in A. A repulsion term, β/r^n, which would raise the ionic curve slightly has been neglected. From Mulliken's discussion[1] of such a term in the case of LiH it appears that in KH for r near 5A, where the strong interaction occurs, the correction would raise the ionic curve not more than a few hundredths of an electron volt.

The relation of the actual potential curve and the ion-pair curve in Fig. 4 supports Mulliken's theory as to the anomalous character of the excited state. The test is made less critical by the fact that the excited state does not dissociate into ions but, due presumably to a second interaction, into K (^2P) and H (^2S). Hence the excited state curve must cross the theoretical ionic curve instead of approaching it asymptotically as the theory would require if a single interaction occurred.

We acknowledge with gratitude assistance in the computations by Mr. David Beiler.