

figurations and Table II lists the positions of 44 of these terms. This completes the location of the more important low terms of this isoelectronic sequence up to Co VI. In the ions of the VII and somewhat higher stages of ionization of this row

of the periodic table the terms of the $3s^23p^63d^{n-1}4p$ configuration become mixed with and distorted by the terms of the $3s^23p^53d^{n+1}$ configuration. This renders the study of these isoelectronic sequences beyond the VI stage difficult and uncertain.

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The Absorption Spectrum of Caesium Hydride

G. M. ALMY AND M. RASSWEILER

Department of Physics, University of Illinois, Urbana, Illinois

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A $^1\Sigma \rightarrow ^1\Sigma$ molecular spectrum of caesium hydride has been photographed in absorption with a three meter glass prism spectrograph. The spectrum is of the many lines type and the observed part lies between 4550A and 6250A. In the longer wave-lengths the bands are masked by a system of Cs_2 bands. The CsH system consists of 31 two-branch bands falling into three v' progressions. There is an additive uncertainty in the v' -numbering. The rotational and vibrational constants have been calculated for the two electronic states. B_v' and $\Delta G'$ show the anomaly characteristic of alkali hydrides, rising with increasing v' to a maximum and then falling off. The heats of dissociation are 1.10 and 1.96 volts for the excited and ground states. Potential energy curves are drawn and it is shown that Mulliken's explanation for the anomalous behavior of the excited states of alkali hydrides fits nicely in the case of CsH.

THE molecular spectra of LiH^1 , NaH^2 and KH^3 have already been extensively investigated both in absorption and emission. They are all of the many lines type and in each case the spectrum has been ascribed to a $^1\Sigma \rightarrow ^1\Sigma$ transition. This system of LiH lies mostly between 3000A and 4500A, that of NaH between 3500A and 5000A, and that of KH between 4100A and 6600A. The determination of the heats of dissociation has indicated in each case that the products of dissociation from the ground state are a normal hydrogen atom and a normal alkali atom, and from the excited state are a normal hydrogen atom and an alkali atom in the first excited 2P state. The alkali hydrides are of particular interest on account of the anomalies which characterize their excited states. Both B_v' and $\Delta G'$ rise to a maximum then begin to fall off instead of decreasing steadily with increasing v' .

This paper is an account of a similar spectrum of CsH which has been photographed in absorption and lies between 4500A and 6250A. Analysis discloses the same anomalies as have been found in the other alkali hydrides.

EXPERIMENTAL PROCEDURE

The CsH absorption column was formed in a heavy walled steel tube 140 cm in length and 2.5 cm in internal diameter. A taper grease joint near one end made it easy to open the tube for cleaning and loading. Welded side tubes at the ends provided for connection to vacuum pumps, hydrogen supply, manometer and escape valve for excess gas. Pyrex windows were waxed to the ends. Water jackets kept the ends cooled. The tube was heated with nichrome coils in separately controlled units so that the ends of the heated section could be maintained at a higher temperature than the center. This somewhat retarded the diffusion of the vapor to the cool ends of the tube. Temperatures were measured at the center by means of a chromel-alumel thermocouple.

¹F. H. Crawford and T. Jorgensen, Jr., *Phys. Rev.* **49**, 745 (1936). Contains complete references to earlier literature.

²T. Hori, *Zeits. f. Physik*, **62**, 352 (1930); **71**, 478 (1931).

³G. M. Almy and C. D. Hause, *Phys. Rev.* **42**, 242 (1932). T. Hori, *Memoirs Ryojun College of Engineering* **6**, 1 (1933).

The tube was loaded by pushing to its center a small iron boat containing metallic caesium under carefully dried xylol. The xylol was then pumped off and dry hydrogen admitted to atmospheric pressure. As heating progressed there first appeared at about 300°C the 4550A and 6250A systems of Cs₂ and the 5370A system of NaCs. These three systems almost completely occupied the visible region until a temperature of 550°C was reached. At this point all but the 6250A system of Cs₂ faded out and gave place to the CsH spectrum. Exposure time was limited to a maximum of 30 minutes by the diffusion of CsH to the water jackets where it condensed in white cotton-like masses and choked the tube. The spectrum was photographed with a Hilger three-meter spectrograph, with optical system of three

prisms and achromatic lens, which had a dispersion of 3 to 10A/mm in the region used.

ANALYSIS OF THE BAND SYSTEM

The CsH spectrum is of the many lines type, and shows no heads or regularities on casual inspection. This is because the heads are very near the origins and because the bands overlap a great deal. Under these conditions it was necessary to begin with the rotational analysis and proceed to the vibrational analysis after the origins had been calculated from the rotational data.

As a beginning, a large number of branches were picked out by the second difference criterion, until one (the 9,0) was found which could

TABLE I. Band origins as interpolated from wave-length data and, in parentheses, as calculated from Eq. (3). Rotational constants and vibrational intervals.

| B_v' | $D_v' \times 10^4$ | $\frac{B_v''}{D_v''} \times 10^4$ | 2.681 | 2.621 | 2.567 | $\Delta G'$ |
|--------|--------------------|-----------------------------------|------------|------------|------------|-------------|
| | | | 1.01 | 0.98 | 1.02 | |
| | | v' | $v''=0$ | 1 | 2 | |
| 1.138 | 0.85 | 0 | | | 16,360.4 | 214.4 |
| 1.145 | 1.01 | 1 | | 17,415.3 | (16,363.6) | |
| 1.154 | 0.80 | 2 | 18,504.0 | (17,416.3) | 16,574.8 | 223.0 |
| 1.165 | 0.87 | 3 | (18,503.8) | 17,638.2 | (16,576.0) | |
| 1.170 | 0.84 | 4 | 18,734.0 | (17,638.3) | 16,797.9 | 230.1 |
| 1.170 | 0.85 | 5 | (18,733.7) | 17,868.3 | (16,798.0) | |
| 1.165 | 0.725 | 6 | 18,970.0 | (17,868.7) | 17,028.1 | 236.0 |
| 1.159 | 0.74 | 7 | (18,970.0) | 18,104.4 | (17,027.9) | |
| 1.153 | 0.74 | 8 | 19,211.0 | (18,104.2) | 17,264.8 | 241.0 |
| 1.144 | 0.70 | 9 | (19,210.9) | 18,345.4 | (17,264.0) | |
| 1.136 | 0.69 | 10 | 19,456.1 | (18,345.4) | | 245.0 |
| 1.124 | 0.66 | 11 | (19,455.9) | 18,590.2 | | 247.7 |
| 1.116 | 0.70 | 12 | 19,703.8 | (18,590.4) | | 249.7 |
| 1.108 | 0.72 | 13 | (19,703.5) | | | 251.0 |
| 1.093 | 0.66 | 14 | 19,953.5 | | | 251.5 |
| 1.079 | 0.61 | 15 | (19,953.2) | | | 251.9 |
| 1.067 | 0.66 | 16 | 20,204.5 | | | 250.6 |
| 1.052 | 0.59 | 17 | (20,204.2) | | | 249.5 |
| | | | 20,456.0 | | | 247.8 |
| | | | (20,455.9) | | | 246.0 |
| | | | 20,707.9 | | | 243.1 |
| | | | (20,707.7) | | | |
| | | | 20,959.4 | | | |
| | | | (20,959.1) | | | |
| | | | 21,210.0 | 20,344.7 | | |
| | | | (21,209.8) | (20,344.3) | | |
| | | | 21,459.5 | 20,594.2 | | |
| | | | (21,459.4) | (20,593.9) | | |
| | | | 21,707.4 | 20,842.0 | | |
| | | | (21,707.3) | (20,841.8) | | |
| | | | 21,953.3 | 21,088.2 | | |
| | | | (21,953.3) | (21,087.8) | | |
| | | | | 21,331.3 | | |
| | | | | (21,331.2) | | |
| | | $\Delta G''$ | 865.5 | 840.3 | | |

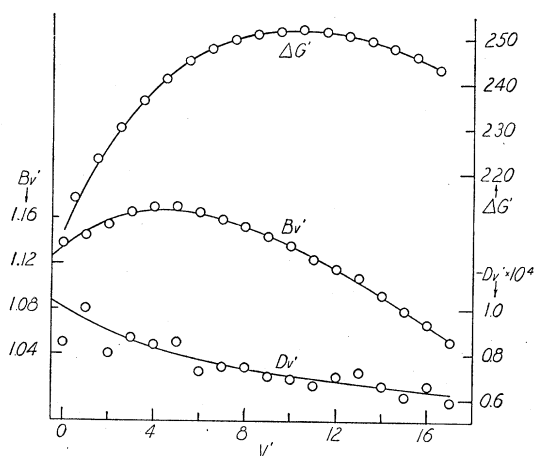


FIG. 1. B_v' , D_v' , $\Delta G'$ for excited state of CsH. Solid B_v' curve is from Eq. (2); solid $\Delta G'$ curve is from first differences of G' in Eq. (3); solid D_v' curve is estimated best fit to experimental points.

be traced through its origin and the rotational quantum numbers assigned. It was then possible to determine the combination differences (1) for this band.

$$\begin{aligned} \Delta_2 F' &= R(K'') - P(K''); \\ \Delta_2 F'' &= R(K'' - 1) - P(K'' + 1). \end{aligned} \quad (1)$$

Since all the bands in a v' progression have the same values of $\Delta_2 F''$ and all those in a v'' progression have the same values of $\Delta_2 F'$, it was easy to determine the numbering and character of the other branches which had been picked out.

Enough bands had then been found so that a good idea of the vibrational intervals could be formed, and the rest were found by predicting on the basis of the intervals and checking up with the combination differences. In this way 31 bands were located. The extensive frequency and combination difference tables are not included here, but are available to anyone interested in them. About 90 percent of the lines were assigned and the remainder were of very low intensity so that the system certainly consists of two-branch bands which arise from a ${}^1\Sigma - {}^1\Sigma$ transition. It thus corresponds to the similar systems of LiH, NaH, and KH which have been assigned to $p\sigma^1\Sigma - s\sigma^1\Sigma$ transitions.

The rotational constants were obtained by a graphical method. For each vibrational state, $\Delta_2 F_v / (4K + 2)$, averaged over the observed

bands, was plotted against $(K + \frac{1}{2})^2$. A straight line was fitted to each of these plots, whose slope is $2D_v$, and whose intercept is B_v . B_v and D_v are listed in Table I and plotted for the upper state in Fig. 1. Only three vibrational levels were observed in the lower electronic state, for which linearly decreasing values of B_v'' and nearly equal values of D_v'' were obtained. D_e'' is taken to be the mean of these, or 1.00×10^{-4} ; exactly the same D_e'' is obtained from the Kratzer relation, $D_e = 4B_e^3 / \omega_e^2$.

As in the other alkali hydrides B_v' at first increases with v' , then decreases. The graphically determined values of B_v' were fitted to a polynomial in $(v + \frac{1}{2})$ by least squares with the result,

$$\begin{aligned} B_{v'} &= 1.1257 + 0.01851(v' + \frac{1}{2}) \\ &\quad - 0.002457(v' + \frac{1}{2})^2 + 0.0000897(v' + \frac{1}{2})^3 \\ &\quad - 0.00000129(v' + \frac{1}{2})^4, \end{aligned} \quad (2)$$

which is plotted as the solid curve in Fig. 1. From this equation B_e' is 1.126, α_e' is 0.0185.

The graphical determination of D_v' is not very precise especially for low v' , but the results, plotted in Fig. 1, show a nonlinear decrease (in the magnitude of D_v') with increasing v' , as has been found in the lighter alkali hydrides. D_e' , obtained by extrapolating this curve to $v' = -\frac{1}{2}$, is -1.04×10^{-4} , in disagreement with the theoretical $D_e' = -4B_e'^3 / \omega_e'^2 = -1.41 \times 10^{-4}$. This disagreement may possibly be due to an error in v' -numbering.⁴

Next the origins of the bands were calculated from a few good lines, chosen, when available, near the origin of each band. These origins and the vibrational intervals (ΔG) are given in Table I. $\Delta G'$ is plotted in Fig. 1. The values of $\Delta G'$ have been fitted to a polynomial by least squares and the result incorporated in the following expression for the band origins,

$$\begin{aligned} \nu_0(v', v'') &= \nu_e + G'(v' + \frac{1}{2}) - G''(v'' + \frac{1}{2}) \\ &= 18,409.8 + [200.94(v' + \frac{1}{2}) \\ &\quad + 6.336(v' + \frac{1}{2})^2 - 0.3789(v' + \frac{1}{2})^3 \\ &\quad + 0.01157(v' + \frac{1}{2})^4 - 0.000172(v' + \frac{1}{2})^5] \\ &\quad - [890.7(v'' + \frac{1}{2}) - 12.6(v'' + \frac{1}{2})^2]. \end{aligned} \quad (3)$$

⁴ Crawford and Jorgensen (reference 1) find in LiH (1) that $-D_v'$ rises very rapidly with decreasing v' at low v' , much more rapidly than $4B_v'^3 / \omega_e'^2$, and (2) that there is no difference between the theoretical and experimental values of D_e' .

The expression for $\Delta G'$ is represented by the solid curve in Fig. 1 and fits nicely the experimental points except for $v'=0$ and 1. The band origins calculated from the above equation agree, generally within $\pm 0.3 \text{ cm}^{-1}$, with those in Table I except, again, for the bands for which $v'=0$ and 1. The calculated origins are written in parentheses in Table I.

Since the bands from the lower vibrational levels of the excited state should be given the greatest weight in the determination of ω_e' and $x_e'\omega_e'$ and since the expression for G' in the above equation does not fit the lower vibrational levels, a separate least squares polynomial to fit the first five intervals $\Delta G'$ was calculated. The result,

$$\begin{aligned} \Delta G'(v'+\frac{1}{2}) &= \omega_e' - 2x_e'\omega_e'(v'+1) \\ &\quad + 3y_e'\omega_e'(v'+1)^2 + \dots \\ &= 204.0 + 11.40(v'+1) \\ &\quad - 1.050(v'+1)^2 + 0.050(v'+1)^3, \end{aligned} \quad (4)$$

fits the observed intervals perfectly. From the coefficients in this equation, $\omega_e' = 204.0$, $x_e\omega_e = 5.70$. These constants have been used in calculating the potential energy curve near its minimum.

There is further uncertainty in the exact values of the upper state constants due to the fact that the v' -numbering is not definitely established. A Cs_2 system which begins at 6250Å prevented the extension of the system to sufficiently long wave-lengths to fix definitely the $v'=0$ progression. The assignment could be fixed by a comparison with the CsD spectrum.

The rotational and vibrational constants of CsH are listed in Table II.

TABLE II. Constants of states of CsH, given in cm^{-1} except where units are specified.

| | LOWER STATE | UPPER STATE |
|----------------------|------------------------|------------------------|
| B_e | 2.709 | 1.126 |
| D_e | -1.00×10^{-4} | -1.04×10^{-4} |
| α_e | 0.057 | -0.0185 |
| r_e | 2.49Å | 3.86Å |
| ω_e | 890.7 | 204.0 |
| $x_e\omega_e$ | 12.6 | 5.70 |
| Heat of dissociation | 1.96 ev | 1.10 ev |

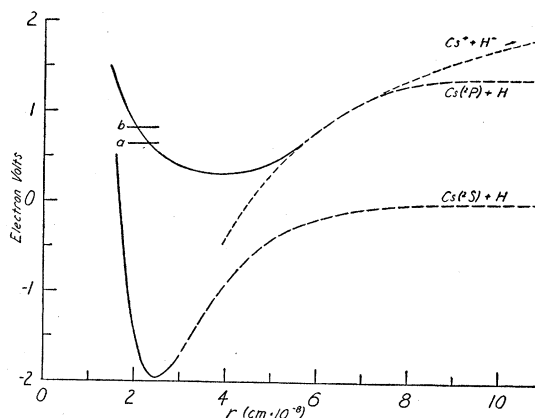


FIG. 2. Potential energy curves for two states of CsH. Normal state: for $r < 3.0\text{Å}$, $U(r) = a_0\xi^2(1 + a_1\xi + a_2\xi^2)$ where

$$\begin{aligned} \xi &= (r - r_e)/r_e, \quad a_0 = \omega_e^2/4B_e = 9.032 \text{ ev}, \\ a_1 &= -[1 + (\alpha_e\omega_e)/6B_e^2] = -2.153 \text{ ev}, \\ a_2 &= (5/4)a_1^2 - (2/3)(x_e\omega_e)/B_e = 2.694 \text{ ev}. \end{aligned}$$

For $r > 3.0\text{Å}$, $U(r) = D_e[1 - e^{-a(r-r_e)}]^2$, where $D_e = 1.96 \text{ ev}$, $a = (8\pi^2cx_e\omega_e\mu/h^2)^{1/2} \text{ cm}^{-1} = 8.67 \times 10^7$, r in cm. Upper state: for $r < 5.5\text{Å}$, power series $U(r)$ with $a_0 = 1.141$, $a_1 = -0.5030$, $a_2 = 3.694$, from constants in Eq. (4). For $r > 5.5\text{Å}$, the upper state is required to go smoothly into the $\text{Cs}^+ + \text{H}^-$ curve at intermediate r , but finally to dissociate into $\text{Cs}(^2P) + \text{H}(^2S)$. The $\text{Cs}^+ + \text{H}^-$ curve is represented at this large separation as a pure Coulomb curve and is given, in ev, by $U(r) = 3.15 - 14.3/r$. The height marked a corresponds to the maximum of the ΔG curve in Fig. 1; b locates the highest observed vibrational level.

HEATS OF DISSOCIATION AND POTENTIAL ENERGY CURVES

The ground state shows a normal behavior of rotational and vibrational constants as in the case of other alkali hydrides. The heat of dissociation, D_e'' , of this state is taken to be $\omega_e'^2/4x_e''\omega_e''$ or 1.96 ev, which, to judge from experience with other molecules, is an upper limit. In the upper state the anomalous behavior of the vibrational intervals prevents a reliable estimate of D_e' by extrapolation. The state is followed 18 levels or about 0.52 ev, but at this energy $\Delta G'$ is not much beyond its maximum (Fig. 1). A linear extrapolation of $\Delta G'$ to convergence indicates that an upper limit of D_e' is about 1.7 ev. Extrapolation of the least squares expression for $\Delta G'$ to its first zero leads to convergence at about 0.9 ev, which is probably too low because of the strong negative terms in the expression required in and characteristic of the region of anomalous behavior. D_e' in all probability lies between these limits; this enables one

to say that the upper state dissociates into a Cs atom in a 2P state, and normal H . Hence, if one assumes $D_e''=1.96$ ev, that the upper state dissociates into $Cs(^2P)$ and normal H and that the v' -numbering is correct one finds $D_e'=D_e''+(^2P-^2S)_{Cs}-v_e=1.96+1.41-2.27=1.10$ ev.

On this basis the potential energy curves in Fig. 2 have been drawn. The lower state is represented by a power series in $(r-r_e)/r_e$ for $r<3.0A$ and by a Morse curve for larger r . The upper state is represented by a power series for $r<5.5A$. For larger r use is made of Mulliken's explanation⁵ of the anomaly in the upper states of the alkali hydrides. Although he makes detailed application only to LiH, he concludes from the similar behavior of the other alkali hydrides that in each of these molecules the two observed states are mainly the result of an interaction between two first approximation $^1\Sigma^+$ states, one derived from unexcited neutral atoms and the other from the ionic pair, in this case Cs^+ and H^- . The result of this interaction is to push apart the two states (which would cross if there were no interaction) and to shape the upper one in such a way as to give an unusual set of vibrational and rotational constants. The chief difference from the usual potential energy curve is that the right side ($r>r_e$) rises more rapidly; this is due to its tendency to go into the relatively steep ionic curve.

Although the potential energy curves in Fig. 2

fit together to form a consistent scheme and are probably correct in the main, their quantitative correctness is in doubt. In the first place, there may be an approximate cancelation of errors in the heat of dissociation of the ground state and in v_e , the origin of the system, the latter arising from a possible error in v' -numbering. That is to say, D_e'' and v_e if in error, are probably both too large; they may be reduced by the same amounts without disturbing the consistency of the potential energy curves. In the second place, Mulliken's suggestion that the upper state should extrapolate smoothly into the ionic curve may not be a valid criterion for plotting the potential energy curve for intermediate r . The potential energy curve for the upper state of LiH has recently been calculated by Rosenbaum⁶ with the Klein-Rydberg method from Crawford and Jorgensen's data. He finds that the upper state crosses the Coulomb ionic curve instead of approaching it asymptotically and concludes that the second interaction mentioned above (near $Li(^2P)+H(^2S)$) is much larger than Mulliken had supposed from qualitative estimates. If the same situation holds in CsH (in which case this interaction must occur at the large interatomic distance of about 7A) the requirement that the upper curve go smoothly into the Cs^+H^- curve is not a valid criterion for determining the form of the upper state curve at intermediate values of r .

⁵ R. S. Mulliken, Phys. Rev. 50, 1028 (1936).

⁶ E. J. Rosenbaum, J. Chem. Phys. 6, 16 (1938).