

## The Emission Spectrum of Molecular Hydrogen in the Extreme Ultraviolet

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### Experimental procedure and results

A new grazing incidence vacuum spectrograph containing a two meter grating, designed by Professor H. E. White and built in the shop of the University of California Physics Department, has been used to photograph more than 2200 lines in the emission spectrum of molecular hydrogen between 1375A and 810A. The known spectrum of this molecule has thus been extended about 200A toward shorter wave-length and more than 1400 new lines have been obtained.

### Identification of lines

The  $2p^1\Sigma - 1s^1\Sigma (B-A)$  band system has been extended so that a number of bands ending on the three lowest vibrational levels of the normal electronic state are now included. A new analysis of the bands of the  $2p^1\Pi_{ed} - 1s^1\Sigma$  system has also been made. Observed and calculated wave numbers are given for all identified lines. Except in the case of perturbed lines these two values agree always within the probable error of experiment (about  $2 \text{ cm}^{-1}$ ).

### The $1s^1\Sigma$ state

Values of the molecular constants for each observed vibrational level in the normal  $1s^1\Sigma$  state have been calculated and tables of the rotational energy function,  $F$ , have been constructed. The new values of  $B$  fall regularly upon a smooth  $B_v : v$  curve, so that it is no longer necessary to assume that a perturbation exists in the  $v=0$  vibrational level. This  $B_v : v$  curve has, however, a positive curvature for low values of  $v$  in contradistinction to the known negative curvature for higher values of  $v$ . The new  $\Delta G_v : v$  curve is also found to be smooth and of the same general shape as the  $B_v : v$  curve.

### The $2p^1\Sigma$ state

The available data on the  $2p^1\Sigma$  state from bands in the visible spectrum given by Richardson and Davidson have been combined with the ultraviolet data for calculation of

the rotational constants. The value of  $B_0$  thus obtained agrees with that given by these authors. The  $B_v : v$  curve for this state is found to have a decided positive curvature for low values of  $v$ , the curvature becoming much less as  $v$  increases. The new and independent values of  $\Delta G_v$  agree to within  $0.4 \text{ cm}^{-1}$  with those given by Richardson and Davidson. Tabulated values of the rotational energy function are given.

### The $2p^1\Pi_{ed}$ state

Because of the  $\Lambda$ -type doubling in this state we find two "effective" values of each of the rotational constants  $B$ ,  $D$  and  $F$ . The true value of  $B$  is, in our case, the effective  $B$  given by the  $c$  component levels. The values of  $B_v$  for these latter levels fall quite regularly on a smooth  $B_v : v$  curve. On the other hand, the  $B_v$  values derived from the  $d$  component levels do not lie on any smooth curve. This is due to a number of perturbations in the  $d$  component levels. Besides a number of ordinary rotational perturbations there is one apparent vibrational perturbation of  $10.4 \text{ cm}^{-1}$  in the  $v=3$  state.

### Values of the constants

Values of  $B_e$  for the  $1s^1\Sigma (A)$ ,  $2p^1\Sigma (B)$  and  $2p^1\Pi_{ed} (C)$  states are found to be 60.8715 (60.587), 19.987, and 31.288 ( $30.065$ )  $\text{cm}^{-1}$ , respectively. Similarly the values of  $\Delta G_e$  for these states are 4417.9 (4371.), 1358.33, and 2468 (2444)  $\text{cm}^{-1}$ , respectively. The value of  $\nu_e$  for the  $2p^1\Sigma - 1s^1\Sigma$  system is  $91,708 \text{ cm}^{-1}$  and the frequency of the  $0-0$  band is  $\nu_{00} = 90,206.1 \text{ cm}^{-1}$ . Corresponding values for the  $2p^1\Pi_{ed} - 1s^1\Sigma$  system are  $\nu_e = 100,049 \text{ cm}^{-1}$  and  $\nu_{00} = 99,087.4 \text{ cm}^{-1}$ . These new values differ appreciably in some cases from the best previous results (as given in parentheses above) and these changes are due to many new assignments and reassignments of lines as well as to the reinterpretation of the apparent perturbation in the  $v=0$  level of the normal state.

### INTRODUCTION

THE secondary or molecular spectrum of hydrogen has been the subject of considerable investigation. The extensive and accurate measurements of wave-lengths in the near infrared, visible and near ultraviolet made by Gale, Monk and Lee have been used by Richardson and his students to obtain extensive infor-

mation concerning many excited electronic states of hydrogen. In order to evaluate the constants of the normal state of the molecule, the extreme ultraviolet spectrum must be studied.

Many investigators, including Lyman,<sup>1</sup> Wer-

<sup>1</sup> T. Lyman, *The Spectroscopy of the Extreme Ultraviolet* (1914).

ner,<sup>2</sup> Witmer,<sup>3</sup> Hori,<sup>4</sup> Dieke and Hopfield,<sup>5</sup> Schaafsma and Dieke,<sup>6</sup> and Hyman,<sup>7</sup> have searched for hydrogen bands in the extreme ultraviolet until almost a thousand lines distributed among nearly a hundred bands have been photographed.

All these data have led to considerable knowledge concerning the energy states and the molecular constants of hydrogen. However, only one band has been observed, by Hori,<sup>4</sup> having as a final state the lowest vibrational level ( $v=0$ ) of the normal electronic state of the molecule and only six of the analyzed bands are found to have  $v=1$  or  $v=2$  as their final states. Moreover, in each of these bands the number of lines observed was small, and accurate values of their wavelengths could not be obtained. The more accurate data of Hyman did not include any lines from bands belonging to the three lowest vibrational states of the molecule.

The analysis of previously observed emission bands in the extreme ultraviolet spectrum has been carried out by Hori,<sup>4</sup> Dieke and Hopfield,<sup>5</sup> Schaafsma and Dieke,<sup>6</sup> and Hyman.<sup>7</sup> It has been shown by these investigators that all of the bands are associated with two excited electronic states of the molecule. Dieke and Hopfield<sup>5</sup> tentatively called these the *B* and *C* states, the normal level being designated the *A* state. It is now known<sup>8</sup> that the normal level is a  $(1s\sigma)^2S^1\Sigma$  state, and that the *B* and *C* levels are respectively  $(1s\sigma)(2p\sigma)P^1\Sigma$  and  $(1s\sigma)(2p\pi)P^1\Pi_{cd}$  states. The designations of these states are usually abbreviated as follows  $1s^1\Sigma$ ,  $2p^1\Sigma$  and  $2p^1\Pi_{cd}$ . It is to be noted that Richardson and his students have published a long series of papers giving bands in the visible spectrum having the two latter levels as their final states.

The theoretical importance of the hydrogen molecule, as well as certain questions concerning the constants for the lowest vibrational states of

the normal electronic level, made it seem worth while to try to obtain new bands in the extreme ultraviolet spectrum. In addition it was thought that bands might be found having different initial electronic states from the two to which all previous bands belonged.

In the investigation here described a large number of new bands was found and the analysis of a number of them has led to much more complete data on the three lowest electronic states of the molecule than have been heretofore available.

## EXPERIMENTAL PROCEDURE

### The spectrograph

In the vacuum region the method of grazing incidence, applied to the construction of grating spectrographs, has been found to possess several advantages over the older types of mounting which featured nearly normal incidence of the light upon the grating. Chief of these advantages are the comparatively much greater dispersion and the greatly increased reflecting power of the grating.

The spectrograph used in the present investigation was designed by Professor H. E. White and constructed in the shop of the University of California Physics Department. It contains a 2-meter concave grating, having a ruled surface of 8 by 5 cm and approximately 567 ruled lines per mm. The grating was ruled at the National Physical Laboratory and was obtained from Adam Hilger Company. A schematic diagram of the instrument is shown in Fig. 1. The

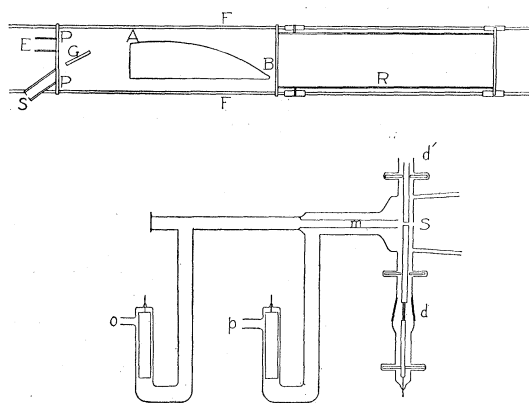


FIG. 1. Schematic diagram of spectrograph and discharge tube.

<sup>2</sup> S. Werner, Proc. Roy. Soc. A113, 107 (1926).

<sup>3</sup> E. E. Witmer, Proc. Nat. Acad. Sci. 12, 338 (1926).

<sup>4</sup> T. Hori, Zeits. f. Physik 44, 838 (1927).

<sup>5</sup> G. H. Dieke and J. J. Hopfield, Zeits. f. Physik 40, 299 (1926); and Phys. Rev. 30, 400 (1927).

<sup>6</sup> A. Schaafsma and G. H. Dieke, Zeits. f. Physik 55, 164 (1929).

<sup>7</sup> H. H. Hyman, Phys. Rev. 36, 187 (1930).

<sup>8</sup> See O. W. Richardson, Proc. Roy. Soc. A126, 487 (1930).

slit  $S$ , the grating  $G$ , and the plateholder  $AB$  are all placed on the usual Rowland circle. The receiver  $R$  is a drawn brass tube 8 inches in diameter and about 36 inches long. As indicated in the diagram, the receiver tube is mounted on wheels fitting a track  $F$  so that the tube may easily be fitted against the end plate  $P$ . A vacuum-tight connection is made by means of a rubber gasket. The spectrograph is evacuated through the air outlet  $E$  by means of a double stage mercury condensation pump backed by a Cenco Hyvac. The design is such that light is incident on the grating at an angle of about  $82.5^\circ$ . Lines having wave-lengths from the very shortest up to about  $1375\text{\AA}$  may be photographed in the first order spectrum.

With the instrument in its best adjustment, remarkably good definition and resolving power can be obtained, as may be seen by examination of the reproductions of two typical spectrograms shown in Fig. 2. The actual resolving power attained in the first order spectrum was about 30,000. The total number of ruled lines on the grating is about 45,000. This last number is not, however, the theoretical resolving power since, as shown by Mack, Stehn and Édlen,<sup>9</sup> the optimum width of a grating at large angles of incidence may be considerably less than the width ordinarily ruled on the grating. The data given by these authors show that in our case the theoretical resolving power of the grating was practically attained. It should be noted also that nonsymmetrical ghosts appeared near each of the very strong lines obtained in this investigation. In accordance with the theory of Mack, Stehn and Édlen, it is now thought that these would not have appeared had the aperture of the grating been reduced to its optimum value.

### The source

The best development of the bands in the extreme ultraviolet spectrum of  $\text{H}_2$  is found to be attained in a rather long discharge tube (total length about 80 cm), the inside of which is ground rough. As was noted by Hyman,<sup>7</sup> the grinding of the discharge tube serves also to suppress the continuous spectrum of hydrogen.

<sup>9</sup> Mack, Stehn and Édlen, *J. Opt. Soc. Am.* **22**, 245 (1932).

The design of the tube is indicated in Fig. 1. It may be seen that this design permits the discharge to be brought very near the slit, and thus serves to insure the full surface of the grating being illuminated as well as to reduce absorption in the discharge tube itself. The electrodes are of aluminum and the tube is of Pyrex of inside diameter about 11 mm, except for the constricted portion  $m$  near the slit. This is reduced to about 6 mm inside diameter.

In operation there exists a continuous leak of hydrogen from the discharge tube through the very narrow slit into the spectrograph. To compensate for this, a continuous flow of hydrogen is maintained through the tube. The hydrogen flows from an electrolytic generator through a variable leak<sup>10</sup> of the type devised by Hopfield, then through drying tubes of calcium chloride and phosphorus pentoxide, and finally into the discharge tube through the inlet  $o$ . A pumping system, separate from that used to evacuate the spectrograph itself, maintains the flow by removing the gas through the tube  $p$ .

As a source of power a one kw 25,000 volt transformer was found to be sufficient. The current through the discharge tube may be estimated at about 30 milliamperes. It may be noted that in the previous investigations of Dieke and Hopfield, and of Hyman, current densities up to 10 times that used in the present investigation were employed. It is thought that the greater number of bands observed in the present work, as well as the extension of the spectrum to a shorter wave-length limit, is due jointly to the maintenance of the discharge at a somewhat lower pressure, to the much better vacuum attained in the receiver (certainly lower than  $10^{-4}$  mm of Hg) and to the high reflecting power of the grating at grazing incidence.

### The comparison spectrum

Investigations in the extreme ultraviolet region of the spectrum have been handicapped by a deplorable lack of suitable standards. The design of the present spectrograph does not permit of the superposition of orders in the region of this investigation since the long wave-length limit, as before noted, is at about  $1375\text{\AA}$ . The vacuum

<sup>10</sup> J. J. Hopfield, *J. Opt. Soc. Am.* **12**, 391 (1926).

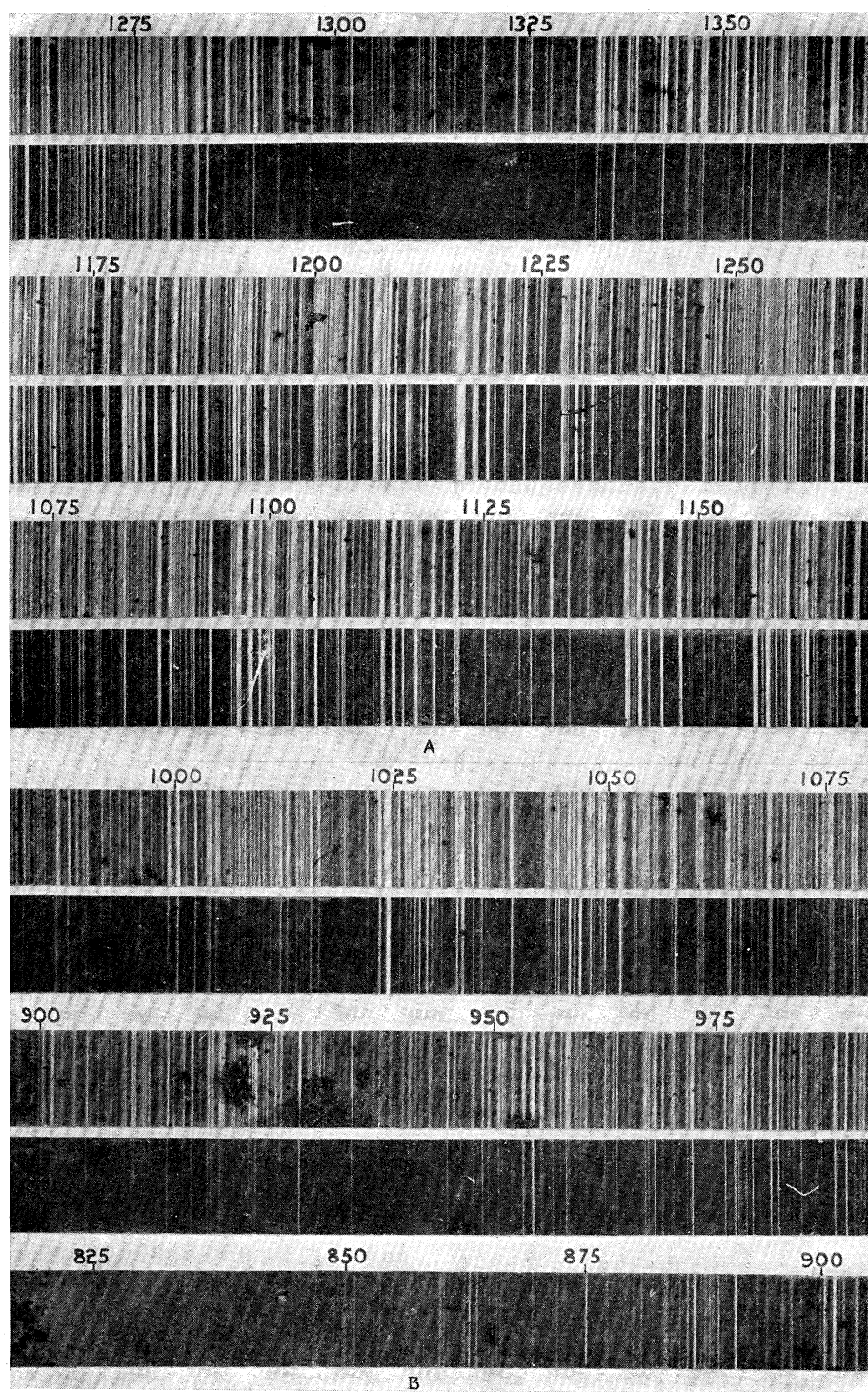


FIG. 2. Enlargements (about  $4\times$ ) of two spectrograms. Exposure times 45 and 25 minutes, respectively.

spark seemed, then, to offer the best possibilities for the production of a sufficient number of lines of known wave-length. Accordingly, a discharge tube was designed in such a way that a pair of aluminum electrodes could be placed between the tube *m* (Fig. 1) and the slit of the spectrograph. These electrodes are carried in two side tubes, *d*, *d'*, in such a manner that by means of a ground glass joint in each they may be adjusted with respect to each other and may be aligned with respect to the slit. The electrodes are placed in series with an external spark gap and in parallel with condensers of about 0.05 microfarad capacity. An interrupter is arranged so that about 25 discharges occur per minute, the sparking time being about 0.8 second. An intermittent spark is necessary so that overheating of the electrodes can be avoided and so that the necessarily low pressure in the tube may be maintained.

It was found that the spark lines of oxygen in the region under investigation could be obtained by using aluminum electrodes. However, the conditions under which they appeared were not easily reproducible. Under certain conditions the oxygen lines disappeared entirely and the spark lines of silicon were found to be brought out with considerable intensity. The wave-lengths of the latter lines, however, are not known with sufficient accuracy for use as standards. If a small stick of carbon be placed in one of the aluminum electrodes, it is found that not only the lines of ionized carbon but also a number of the spark lines of oxygen are easily made to appear in the discharge. There is a sufficient number of these lines so that between 800 and 1375A there is no gap greater than 75A. Usually the distance between lines is much smaller than this. The wave-lengths of the lines may be found in the tables compiled by MacInnes and Boyce.<sup>11</sup> Besides these lines the second, third and fourth members of the Lyman series were available as standards in the present work. The theoretical values of the wave-lengths of the Lyman series lines have been calculated by Penney.<sup>12</sup> The first member of the Lyman series was usually so over-

exposed on the plates obtained by the writer that it could not be used as a standard.

For various reasons it was thought best not to superpose the comparison spectrum upon the plates that showed the H<sub>2</sub> spectrum in its best development. Instead, a rather large number of plates were taken, each showing the comparison spectrum but having various different times of exposure of the hydrogen spectrum. From these plates there were determined the wave-lengths of 35 hydrogen lines to be used as auxiliary standards.

#### Reduction of the plates and experimental results

Measurements of the plates studied were made by use of a 200 mm Gaertner comparator, owned by Professor R. T. Birge. It was found that in a few cases the vacuum spark spectrum was shifted by a small but easily detectable amount with respect to the hydrogen band spectrum. It is thought that this was due to the spark electrodes being in such a position that only part of the grating (and probably not a central part) was illuminated. It would seem necessary in all studies in which such spark spectra are observed to make certain, by measurement of a reasonable number of plates, that the spectrum is not shifted because of unequal illumination of the grating. This effect may be shown to be accentuated considerably by use of the grating at grazing incidence. It may be especially troublesome where, as in the present study, two spectra from different sources are to be superposed.

Another source of possible error in the measurement of wave-length is due to the fact that at grazing incidence not only is the spectrum far from normal, but small irregularities in the curvature of the plate may introduce relatively very large deviations from a smooth dispersion curve. In the present instance it was found that if the dispersion curves were assumed smooth, an error in value of the wave-lengths of more than 0.2A might be made in some cases. It is accordingly thought worthwhile to give a rather detailed description of the method used in reduction of the plates.

For a determination of the wave-lengths of 35 hydrogen lines to be used as auxiliary standards, seven plates showing both vacuum spark and hydrogen discharge spectra were measured. For

<sup>11</sup> J. M. MacInnes and J. C. Boyce, *Wave-lengths of the Extreme Ultraviolet Lines from Gas Discharges* (1930).

<sup>12</sup> W. G. Penney, *Phil. Mag.* 9, 661 (1930).

each of these plates tables were constructed of divided second differences of the wave-lengths of spark lines as a function of comparator readings. From these second differences, wave-lengths corresponding to equal intervals of the comparator scale were interpolated. The method of Birge and Shea<sup>13</sup> could then be applied to the calculation of least square polynomials of the second degree giving wave-length as a function of comparator readings. The differences between the known wave-length of each standard line and the wave-length calculated in this way for the particular plate under consideration could then be plotted as a correction curve. From the least squares equation and the correction curve, the wave-length of each of the 35 auxiliary hydrogen standards was obtained. Comparison of the wave-lengths thus calculated from different plates indicates that the probable error of  $\lambda$  in any case should not be greater than 0.05Å. Application of the combination principle shows that over small intervals, such as the extent of any one band, the relative wave-lengths have probable errors much smaller than 0.05Å but that the probable error of the relative values of  $\lambda$  over great intervals may be as large as 0.05Å.

After determination of  $\lambda$  for the auxiliary standards, all the lines were measured on two plates showing the best development of the H<sub>2</sub> spectrum. Correction curves for these plates were made in the same manner as described above and from the resulting least squares equations, wave-lengths were found of a larger number of lines spaced over intervals of 4 mm or less. It may be shown that over intervals no greater than 4 mm along the plate, linear interpolation introduces no appreciable error in the derived values of  $\lambda$ . The determination of the remaining wave-lengths, which includes more than 2200 lines, was then made by direct linear interpolation. The difference in wave-length of the great majority of lines, as determined from the two separate plates, was less than 0.02Å.

Two typical spectrograms are reproduced in Fig. 2, with a magnification of about 4×. The exposure times for these plates were 45 minutes and 25 minutes, respectively. The first of the

plates contains about 2200 lines (exclusive of ghosts) of which at least 1400 are new. The short wave-length limit is at 810Å as contrasted with a former limit of about 1000Å.

#### ROTATIONAL ANALYSIS

##### Identification of lines

Since the approximate positions of all bands in the  $2p^1\Sigma - 1s^1\Sigma$  and  $2p^1\Pi_{cd} - 1s^1\Sigma$  systems could be determined from previous work, the identification of as many lines as possible was carried out by searching for constant frequency intervals. In accordance with the prevailing notation, these constant frequency intervals may be designated as follows:

$R(K) - P(K) = \Delta_2 F'_K = \text{a constant for all bands}$   
having the same initial vibrational state  
 $v' = \text{constant};$

$R(K-1) - P(K+1) = \Delta_2 F''_K = \text{a constant for } v''$   
constant;

$Q(K) - P(K) = \text{constant for } v' \text{ constant};$

$R(K) - Q(K) = \text{constant for } v' \text{ constant.}$

The latter two conditions are used only for the  $^1\Pi_{cd} - ^1\Sigma$  system. The rule that the second differences of the frequencies of lines in any branch are approximately constant is also very useful. Because of the extremely large number of lines in this spectrum (see Fig. 2) and the fact that there are no superficially evident regularities, chance agreement of frequency intervals is very frequent and in many cases it is only after applying every known test that one can be certain of the proper identification of the lines of a band.

##### The $1s^1\Sigma$ state

As has been noted previously, the data given by Hyman<sup>7</sup> have yielded values of the rotational constants of the normal ( $1s^1\Sigma$ ) state for values of  $v$  equal to or greater than 3. An extrapolation of these data to smaller values of  $v$  has already been made.<sup>14</sup> From Rasetti's data<sup>15</sup> on the Raman effect in gaseous hydrogen, accurate values of the constants for  $v=0$  and  $v=1$  have been calcu-

<sup>13</sup> R. T. Birge and J. D. Shea, University of California Publications in Math. 2, No. 5, 67 (1927).

<sup>14</sup> H. H. Hyman and C. R. Jeppesen, Nature 125, 462 (1930).

<sup>15</sup> F. Rasetti, Phys. Rev. 34, 367 (1924).

TABLE I. Average values of  $\Delta_2 F''$  ( $\text{cm}^{-1}$ ).

$K$	$v=0$	1	2	3	4	5
1		336.52 (4)	319.2 (4)	301.70 (7)	285.33 (9)	268.3 (5)
2		558.04 (5)	528.63 (3)	500.74 (7)	473.65 (11)	445.56 (5)
3	812.0 (3)	772.84 (5)	734.0 (4)	695.17 (7)	654.49 (8)	618.46 (3)
4	1034.42 (4)	981.43 (3)	932.03 (3)	882.64 (7)	832.98 (5)	781.66 (3)
6	1452.1 (2)					

lated.<sup>16</sup> Since the Raman effect data had shown an unexplained deviation in the values of the rotational constant  $B_0$  and the vibrational constant  $\Delta G_{\frac{1}{2}}$  from the smooth extrapolated  $B_v : v$  and  $\Delta G : v$  curves<sup>16</sup> it was desirable to obtain complete data from band spectra on the lower vibrational states and to examine critically all the experimental results.

In Table I are given the values of  $\Delta_2 F$  as obtained in the present work.

The figures in parentheses give the number of individual values on which each average is based. The lines from which each individual value is obtained are listed in Table VII.

Since the spectrograph used did not permit observation of the bands having wave-lengths greater than 1375A, these data were supplemented by data of Hyman<sup>7</sup> in order to obtain values of  $\Delta_2 F$  for  $v$  larger than 3. By the well-known graphical method<sup>17</sup> preliminary values of  $B_v$  were found.  $B_e$  is obtained by a simple extrapolation. The value of  $D_e$  is now found from the theoretical relation:

$$D_e = -4B_e^3/\omega_e^2 \quad (1)$$

where  $\omega_e = \Delta G_{-\frac{1}{2}}$  except for the (negligible) difference between the value of the finite difference and the derivative.

The values of  $D_v$  may be derived from the theoretical relation:

$$D_v = D_e - \beta_e(v + \frac{1}{2}) \quad (2)$$

where<sup>7</sup>

$$\frac{\beta_e}{D_e} = -\frac{\omega_e}{24B_e} \left(\frac{\alpha_e}{B_e}\right)^2 - 5\left(\frac{\alpha_e}{B_e}\right) + 8x_e \quad (3)$$

$2x_e\omega_e$  is the slope of the  $\Delta G : v$  curve at  $v = -\frac{1}{2}$  and  $\alpha_e$  is the corresponding slope of the  $B_v : v$  curve at  $v = -\frac{1}{2}$ .

The value of  $F_e$  is given by the expression

$$F_e = (D_e^2/B_e)(2 - \alpha_e\omega_e/6B_e^2). \quad (4)$$

The value of  $F_e$  may be seen to be very small, although it is not negligible in the case of the present work. The variation in  $F_e$  with  $v$  is however so small<sup>18</sup> that the use of  $F_e$  for  $F_v$  in our work was justified. From these values of  $D_e$  and  $F_e$  better approximate values of  $B_v$  were found.

The preliminary values of all of these rotational constants together with similar constants for the excited  $B$  and  $C$  states of the molecule allowed the values of the rotational energy functions to be obtained for each of the electronic states under consideration. These, in turn, enabled a rigorous check of the placement of lines in the various bands to be made. Corrections were then made in the values of  $\Delta_2 F$  and the analytic method given by Birge<sup>17</sup> was then used for the final calculation of  $B_v$  values. The results of this calculation without smoothing the data, together with the previous best values<sup>7, 14, 16</sup> are given in Table II.

It may be seen that the agreement between the band spectra data of the previous work as given

TABLE II.

$v$	$B_v$ from present work	$B_v$ from Raman effect data	$B_v$ from previous smooth curve <sup>14</sup>
0	59.396	59.354	59.192
1	56.413	56.4035	56.411
2	53.528		53.630
3	50.697		50.834
4	47.870		48.008
5	44.973		45.138
6	42.094		42.210
7	39.134		39.209
8	36.086		36.120
9	32.712		32.930

<sup>16</sup> R. T. Birge and C. R. Jeppesen, Nature **34**, 463 (1930).

<sup>17</sup> See R. T. Birge, National Research Council Bulletin No. 57, *Molecular Spectra in Gases*, pp. 172-4 (1926).

<sup>18</sup> The theoretical expression for  $F_v$  as a function of  $v$  is given by J. L. Dunham, Phys. Rev. **41**, 721 (1932).



in column 3, Table II, and that here obtained is not as good as might be expected. This is due to two factors. In the first place, the placement of a number of lines in the previously analyzed bands<sup>4, 6, 7</sup> has been found to be incorrect. In most cases, it has been found impossible to be certain of the placement of any lines for greater rotational quantum number than  $K=5$  or 6. This is due to the fact that for large values of  $K$  the constants  $D$  and  $F$  contribute a very large amount to the value of the rotational energy function and the theoretical values of these constants which must be used in our calculations progressively become less trustworthy as  $v$  increases. In the second place, it has been found possible in the present work to proceed entirely, in the final calculations, by the more accurate analytical method.<sup>17</sup>

It should be noted that the results for  $B_0$ ,  $B_1$  and  $B_2$  in the third column of Table II were obtained largely by linear extrapolation since the more accurate band spectra data previous to the present work did not extend below the  $v=3$  level. The fact that the extrapolated value of  $B_1$  agreed with the Raman effect value was considered good evidence for the reliability of the linear extrapolation. However, it is now seen that this agreement was largely accidental and was due to the fact that the accepted values of  $B_v$  for  $v$  greater than 3 were too large, by small but appreciable amounts. The Raman effect value of  $B_0$ , however, did not lie upon the smooth extrapolated curve and this was then believed to denote a perturbation in the moment of inertia for the lowest level.<sup>16</sup>

On the other hand, it may be seen that the values of both  $B_0$  and  $B_1$ , as obtained in the present work, are in quite satisfactory agreement with the values obtained<sup>16</sup> from Rasetti's data<sup>15</sup> on the Raman effect. The fact that the agreement between the two values of  $B_0$  is not quite so good as between the  $B_1$  values is due to the lack of data on the  $v=0$  state for lower values of the rotational quantum number  $K$ , and also to the greater amount of data on the  $v=1$  state for nearly all values of  $K$ . The Raman effect values have been adopted in this work since they are somewhat more accurate than the values obtained from band spectra.

It is now found that the values of both  $B_0$  and

$B_1$ , as well as the value of  $B_2$  which has not previously been determined with any accuracy, all lie on a smooth curve with the new values of  $B_v$  for  $v$  larger than 2. Hence we have the important conclusion that it is no longer necessary to assume that the value of  $B_0$  is perturbed.

The new  $B_v : v$  curve, Fig. 3, is found to have a

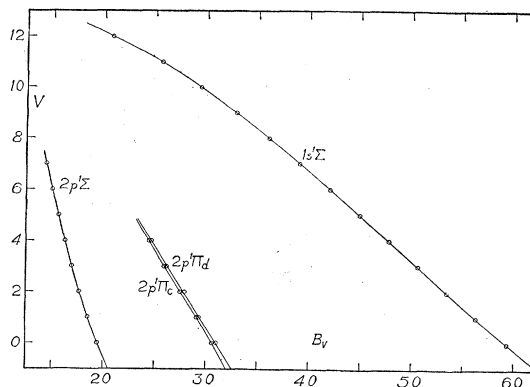


FIG. 3.  $B_v : v$  plot for the  $1s^1\Sigma$  (A),  $2p^1\Sigma$  (B) and  $2p^1\Pi_{cd}$  (C) states.

decided positive curvature for low values of  $v$  in contrast to the negative curvature for high values. From  $v=0$  to  $v=4$ , the values of  $B_v$  are given to well within the probable error by the least squares equation:

$$B_v = 60.8715 - 3.06709(v + \frac{1}{2}) + 0.068393(v + \frac{1}{2})^2 - 0.0065(v + \frac{1}{2})^3. \quad (5)$$

The pronounced positive curvature at  $v=0$  and the negative curvature starting at about  $v=3$  make the  $B_v : v$  function impossible of accurate representation by this type of equation for all values of  $v$ . The extrapolated value of  $B_e$  ( $60.8715 \text{ cm}^{-1}$ ) given by the above equation is the same as that determined by difference tables and also graphically, so that the extrapolation is believed to be trustworthy. The resulting new value of  $I_e = 0.45437 \times 10^{-40} \text{ g cm}^2$  is less by 0.47 percent than that previously published.<sup>14</sup>

Values of the rotational energy function  $F$  for the  $1s^1\Sigma$  state are given in Table VI.

#### The $2p^1\Sigma$ state

For the evaluation of the constants of the  $2p^1\Sigma$  state we have, in addition to the data of the present work, the investigations of the ultra-



violet spectrum mentioned previously and the more accurate data published by Richardson and Davidson<sup>19</sup> who have found bands in the visible spectrum having the level  $2p^1\Sigma$  as their final state. The  $\Delta_2F$  values that result from these data on the visible bands were found to be in all cases consistent with the  $\Delta_2F$  values based on the ultraviolet bands, and the two sets of  $\Delta_2F$  values have therefore been freely combined to give final, most probable values of the various constants.

Both Richardson and Davidson<sup>19</sup> and Hyman<sup>7</sup> have evaluated the moment of inertia for the  $v=0$  level of this state. We wish, however, to evaluate the constants of the molecule for the higher vibrational states so as to be able to give a complete rotational and vibrational analysis of the  $2p^1\Sigma - 1s^1\Sigma$  system.

The procedure outlined for the derivation of constants for the  $1s^1\Sigma$  state should apply also to the  $2p^1\Sigma$  state under consideration. It may be shown, however, that, in the latter case, Eq. (2) cannot be made to give values of  $D_v$  that agree with the experimental data, for any constant values of  $x_e$  and  $\alpha_e$ . While the method about to be described has no obvious theoretical justification, values of  $D_v$  for the  $2p^1\Sigma$  state may be obtained such that, within the limit of the experimental error of the measurements, entirely satisfactory results are secured. Two rigorous checks are required of the  $D_v$  values thus obtained: they must satisfy the analytic method for determination of  $B_v$  values by successive approximations, and they must give rotational energy functions such that every line in a band gives the same value of the origin of the band when the rotational term values are subtracted out.

Let us assume

$$D_v = D_{v-1} + \beta_{v-1}, \quad (6)$$

where

$$\beta_{v-1} = \beta_i = -\frac{1}{6} \frac{\alpha_i^2}{\omega_i} - \frac{20\alpha_i B_i^2}{\omega_i^2} - \frac{32x_i B_i^3}{\omega_i^2}. \quad (7)$$

Eq. (7) is obtained from Eq. (3) by the substitution of the value of  $D_e$  from (1) and the replacing of  $B_e$  by  $B_{v-1}$ . The quantities  $\alpha_{v-1}$  and

$x_{v-1}$  are not assumed constant; instead they represent the slope of the  $B_v : v$  and  $\Delta G_v : v$  curves at any designated values of  $v - \frac{1}{2}$  and are obtained directly from the experimental data. Since the theoretical equation  $D_e = -B_e^3/\omega_e^2$  is true for any kind of binding in the molecule (i.e., independent of the linearity or lack of linearity of the  $\Delta G : v$  and  $B_v : v$  curves) we first get the true value of  $D_e$  and then proceed step by step to obtain each value of  $D_v$  from  $D_{v-1}$  according to the above equations. Values of  $x_v$  and  $\alpha_v$  as functions of  $v$ , as well as the derived values of  $D_v$  are given in Table III.

TABLE III. Values of  $x$ ,  $\alpha$  and  $D$  for the  $2p^1\Sigma$  state.

$v$	$x_{v-1/2}$	$\alpha_{v-1/2}$ (cm <sup>-1</sup> )	$D_v$ (cm <sup>-1</sup> )
0	0.01516	1.077	-0.015838
1	0.01453	0.962	-0.013571
2	0.01402	0.832	-0.011791
3	0.01373	0.720	-0.010416
4	0.01373	0.662	-0.009243
5	0.01388	0.635	-0.008162
6	0.01404	0.605	-0.007179
7	0.01426	0.575	-0.006298

The extrapolated value of  $D_e$  is  $-0.017188$  cm<sup>-1</sup>. The calculated value of  $F_e$  is (from Eq. (4))  $2.916 \times 10^{-5}$  cm<sup>-1</sup>, and as already noted  $F_e$  may safely be used for  $F_v$  in general.

By using these calculated values of  $D_v$  and  $F_v$  it is possible to obtain values of  $4B_v$  from each value of  $\Delta_2F/K + \frac{1}{2}$  by use of the well-known expression for the rotational energy of a  $^1\Sigma$  state. A weighted average of the resulting values of  $4B_v$  for each value of  $v$  was thus obtained. These values of  $4B_v$  differed by such small amounts from the first values obtained directly from the  $(\Delta_2F/K + \frac{1}{2}) : K$  curves that it was deemed unnecessary to calculate new  $D_v$  values and to apply a second approximation. The values of  $B_v$  obtained, from  $v=0$  to  $v=7$ , are as follows: 19.457, 18.482, 17.652, 16.933, 16.265, 15.626, 15.004, 14.410 cm<sup>-1</sup>. The extrapolated value of  $B_e$  is 19.987 cm<sup>-1</sup>. The value of  $B_0$  given above, i.e., 19.457, may be compared with Richardson and Davidson's<sup>19</sup> published value of 19.455. Of course these two values are not independent since, as just noted, Richardson and Davidson's data were used in conjunction with the extreme ultraviolet data for the derivation of the results given above. The comparison does, however,

<sup>19</sup> O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. A123, 54 (1929); also Proc. Roy. Soc. A123, 466 (1929).

show in a simple manner the perfect consistency of the visible and the ultraviolet data for this  $2p^1\Sigma$  state.

The  $B_v$  values obtained as described lie very well on a smooth curve, the least squares solution of which is:

$$B_v = 20.0245 - 1.195559(v + \frac{1}{2}) + 0.1292308(v + \frac{1}{2})^2 - 0.0133636(v + \frac{1}{2})^3 + 0.00053788(v + \frac{1}{2})^4. \quad (8)$$

While this equation fits the data very well from  $v=0$  to 6 it does not give a good extrapolated value of  $B_v$ . This is due to the pronounced curvature of the  $B_v : v$  curve (see Fig. 3) which is such that another form of function than the polynomial is required if one wishes a trustworthy extrapolation.

#### The $2p^1\Pi_{cd}$ states

The analysis of the  $2p^1\Pi_{cd}$  states of  $H_2$  was first carried out by Hori.<sup>4</sup> The more accurate data of the present investigation have shown, however, that a number of his lines were given incorrect quantum assignments. This, together with the fact that his measured wave-lengths are necessarily less accurate, may in part be responsible for his positive values of the rotational constants  $D_v$ , as well as for a value of the moment of inertia of the normal  $1s^1\Sigma$  state that does not agree well with the one later obtained in this laboratory.<sup>14, 16</sup>

Accordingly, a new analysis of the  $2p^1\Pi_{cd} - 1s^1\Sigma$  bands has been made in the present study. The rotational energy function for a  $^1\Pi$  state may be written:<sup>20</sup>

$$F = B_v[(K + \frac{1}{2})^2 - \Lambda^2 + \bar{G}^2] + \varphi_i(K) + D_v[(K + \frac{1}{2})^4 + \dots] + F_v[(K + \frac{1}{2})^6 + \dots], \quad (9)$$

in which  $\varphi_i(K)$  is given by:

$$\varphi_i(K) = \kappa_i + \delta_i(K + \frac{1}{2})^2 + \mu_i(K + \frac{1}{2})^4 + \dots \quad (10)$$

where  $\delta_i \gg \mu_i \gg \dots$  and  $\kappa_i$  is of the same order of magnitude as  $\delta_i$ . The data of the present work show this equation to be correct for the  $2p^1\Pi_{cd}$  state of  $H_2$ . In this case  $\varphi_i(K)$  may be combined with the other terms of Eq. (9) by writing

$$B_i^x = B_v + \delta_i; \quad D_i^x = D_v + \mu_i. \quad (11)$$

Since the constant term  $B_v(\bar{G}^2 - \Lambda^2)$  is small and cannot be separated from the electronic energy of the term, we write Eq. (9) in the form

$$F = B_i^x(K + \frac{1}{2})^2 + D_i^x(K + \frac{1}{2})^4 + F_i^x(K + \frac{1}{2})^6. \quad (12)$$

This is identical with the expression giving the rotational energy for  $^1\Sigma$  states except that here we have the "effective"  $B$ ,  $D$  and  $F$  values,  $B_i^x$ ,  $D_i^x$  and  $F_i^x$  in place of the true  $B_v$ ,  $D_v$  and  $F_v$  that give the value of the moments of inertia and other constants of the molecule.

Van Vleck<sup>21</sup> has shown that in the case of  $^1\Pi$  states the function  $\varphi_i(K)$  has the double form:

$$\varphi_c(K) = -2C + (C + C_2)(K + \frac{1}{2})^2 \dots \text{ and} \quad (13)$$

$$\varphi_d(K) = -2C + (C + C_1)(K + \frac{1}{2})^2 \dots$$

It is also shown by Hill and Van Vleck<sup>22</sup> and by Dieke<sup>23</sup> that in the case of many of the excited states of  $H_2$  and  $He_2$ , where the existence of  $\varphi_i(K)$  is due mainly to an electron in a large orbit of azimuthal quantum number  $l$ ,  $C_2$  equals zero and if  $l=1$ ,  $C$  also equals zero. It is evident that in the case of the  $2p^1\Pi_{cd}$  state of  $H_2$  these conditions are satisfied; hence for this state we have  $\varphi_c(K) = 0$ . One of the two values of  $B_i^x$ , namely  $B_c^x$ , should then equal the true  $B_v$  value for this state, and  $B_d^x$  should equal  $B_v + C_1$ .

This situation is also found in  $He_2$ <sup>23</sup> where a series of  $np$  states ( $n=2$  to 11) is known. In this case  $B_c^x$  remains practically constant throughout the series whereas  $B_d^x$  decreases steadily with increasing  $n$ , due presumably to a variation of  $C_1$  with  $n$ .

According to theory, the  $Q$  branches of our  $^1\Pi - ^1\Sigma$  bands arise from transitions having the  $c$  component levels as their initial states, whereas the  $P$  and  $R$  branches arise from the  $d$  components. Values of the effective constants  $B_i^x$  and  $D_i^x$  have been derived from the data of the present work and their values are given later in the paper.

For the  $d$  component levels  $\Delta_2 F_d$  values, derived from the  $P$  and  $R$  branches, may be obtained from the usual relation:

<sup>21</sup> J. H. Van Vleck, Phys. Rev. **33**, 484 (1929).

<sup>22</sup> E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 270 (1928).

<sup>23</sup> G. H. Dieke, Zeits. f. Physik **47**, 71 (1929).

<sup>20</sup> See R. S. Mulliken, Rev. Mod. Phys. **2**, 100 (1930) and **3**, 102 (1931).

$$\Delta_2 F'' = R(K) - P(K). \quad (14)$$

The wave numbers of these lines are given in Table VII. For the  $c$  components, however, the  $\Delta_2 F$  values cannot be obtained so directly. Our previous analysis has enabled us to get very accurate values of  $F$ , the rotational energy function, for the  $1s^1\Sigma$  level which is the final state for the bands under consideration. Hence the  $\Delta F''$  values are known with considerable accuracy.

From the familiar relation

$$Q(K) = \nu_0 + F_c'(K) - F''(K) \quad (15)$$

we have:

$$Q(K+1) - Q(K) = F_c'(K+1) - F''(K+1) - F_c'(K) + F''(K) \quad (16)$$

and since by definition

$$\Delta F(K + \frac{1}{2}) = F(K+1) - F(K)$$

we have at once from Eq. (16):

$$\Delta F_c'(K + \frac{1}{2}) = Q(K+1) - Q(K) + \Delta F''(K + \frac{1}{2}). \quad (17)$$

Using the observed wave numbers of the  $Q$  branch lines as given in Table VII and using  $\Delta F''$  values derived from the calculated  $F$  values for the normal state of the molecule (Table VI), we are then enabled to obtain  $\Delta F_c$  values for the  $2p^1\Pi_c$  states by means of Eq. (17). The values obtained from Eqs. (14) and (17) are given in Table IV.

TABLE IV.

$K$	$v=0$	1	2	3	4
Average $\Delta_2 F_d'(K)$ values ( $\text{cm}^{-1}$ )					
2	305.33	290.5	276.67	257.4	244.2
3	426.93	401.07	390.95	360.5	330.1
4	542.8	513.4		457.7	
5	661.7				
Average $\Delta F_c'(K + \frac{1}{2})$ values.					
1	122.3	115.9	109.7	104.0	96.63
2	180.23	171.8	162.28	153.46	145.13
3	240.45	227.55	214.68	202.95	192.05
4	295.8	282.40	266.37	250.5	235.4

The semi-graphical method, already used in connection with the calculation of preliminary values of  $B_v$  in the case of the  $2p^1\Sigma$  state, may then be applied to the data of the  $2p^1\Pi_{cd}$  states. It was found immediately that the  $(\Delta_2 F_d/K + \frac{1}{2})$

values did not in some cases fall regularly upon a smooth curve. This, and additional evidence to be presented later, led to the discovery of a number of perturbations in the  $d$  component levels. The  $c$  levels, however, were found to be quite regular.

After obtaining approximate values of  $B_{i^x}$  in the way just described, preliminary values of  $D_{i^x}$  were calculated by the theoretical Eqs. (1), (2) and (3) given previously. The analytic method described by Birge<sup>17</sup> was then applied to the accurate determination of  $B_{i^x}$ . The values of  $B_{c^x}$  (obtained from  $\Delta F_c(K + \frac{1}{2})$  as given in Table IV) were found to fall quite regularly upon a smooth curve, as is shown in Fig. 3. The least squares equation giving  $B_{c^x}$  as a function of  $v$  is:

$$(B_{c^x})_v = 31.288 - 1.31673(v + \frac{1}{2}) - 0.119696(v + \frac{1}{2})^2 + 0.0164167(v + \frac{1}{2}). \quad (18)$$

As mentioned previously the rotational levels belonging to the  $d$  component states contain so many perturbations that accurate values of  $(B_{d^x})_v$  could not be calculated. While it is not possible to determine the form of the  $(B_{d^x})_v$  function because of the irregularity of the data, a straight line seemed to offer the best analytic representation of this function. Accordingly, the following linear equation was found:

$$(B_{d^x})_v = 31.735 - 1.5702(v + \frac{1}{2}). \quad (19)$$

The values of  $B_{i^x}$  as obtained from the data and as calculated from Eqs. (18) and (19) are given together with values of  $D_{i^x}$  in Table V.

The calculated values of  $F_{i^x}$  are, from Eq. (4):  $F_{c^x} = 1.8901 \times 10^{-5} \text{ cm}^{-1}$  and  $F_{d^x} = 1.9702 \times 10^{-5} \text{ cm}^{-1}$ .

Richardson<sup>24</sup> has found also a number of bands in the visible spectrum having  $2p^1\Pi_{cd}$  as the final state. The values of  $B_{i^x}$  for the  $v=0$  state as determined from his data may be compared with those of the present investigation. Richardson does not calculate "effective"  $B$  values, but when the methods used in this paper are applied to his data one obtains  $B_{c^x} = 30.361$  and  $B_{d^x} = 31.063$  for  $v=0$ .

The agreement is seen not to be as good as might be expected. In obtaining the above values from Richardson's data the following

<sup>24</sup> O. W. Richardson, Proc. Roy. Soc. A126, 487 (1929).

TABLE V.  $B_i^x$  values for  $2p^1\Pi_{cd}$  states.

$v$	Obs. $B_c^x$	Calc. $B_c^x$	$D_c^x$	Obs. $B_d^x$	Calc. $B_d^x$	$D_d^x$
$-\frac{1}{2}$						
0	30.599	31.288	-0.020959	31.003	31.735	-0.021001
1	29.113	30.602	-0.020545	29.348	30.950	-0.020197
2	27.485	29.099	-0.019718	27.945	29.380	-0.019393
3	25.931	27.505	-0.018891	26.211	27.809	-0.018589
4	24.432	25.917	-0.018064	24.674	26.239	-0.017785
		24.435	-0.017236		24.669	-0.016981

procedure was followed. From the rotational energy function

$$F = B_i^x(K + \frac{1}{2})^2 + D_i^x(K + \frac{1}{2})^4 + F_i^x(K + \frac{1}{2})^6 \quad (20)$$

we have:

$$\Delta_1 F = (2B_i^x + D_i^x + (3/8)F_i^x)(K + \frac{1}{2}) + (4D_i^x + 5F_i^x)(K + \frac{1}{2})^3 + 6F_i^x(K + \frac{1}{2})^5. \quad (21)$$

Let us write, following the usual analytic method<sup>17</sup>

$$\Delta_1 F^* = \Delta_1 F - (4D_i^x + 5F_i^x)(K + \frac{1}{2})^3 - 6F_i^x(K + \frac{1}{2})^5. \quad (22)$$

Richardson's published  $\Delta_1 F$  values then yield the following values of  $\Delta_1 F^*$ :

$K + \frac{1}{2}$	$\Delta_1 F^*$ ( <i>c</i> states)	$\Delta_1 F^*$ ( <i>d</i> states)
$1\frac{1}{2}$	122.262	124.442
$2\frac{1}{2}$	183.137	186.341
$3\frac{1}{2}$	237.734	247.933

$$\text{But } 2B_i^x = (\Delta_1 F^*/K + \frac{1}{2}) - D_i^x + (3/8)F_i^x. \quad (23)$$

Hence, using each of the above values of  $\Delta_1 F^*$ , one obtains for  $B_c^x$  and  $B_d^x$  the following:

$K + \frac{1}{2}$	$B_c^x$	$B_d^x$
$1\frac{1}{2}$	30.576	31.121
$2\frac{1}{2}$	30.533	31.068
$3\frac{1}{2}$	29.727	31.002

It is seen that the values of both  $B_c^x$  and  $B_d^x$ , instead of being constant, show a distinct downward trend as  $K$  increases, indicating that the values of  $D_i^x$  used are numerically too small. However, the values of  $D_i^x$  used are the values calculated by the equations given previously and furthermore, these same  $D_i^x$  values lead to entirely consistent results when applied to the data of the present paper. It therefore appears

that Richardson's data include some incorrect identifications. Indeed Chalk<sup>25</sup> has published a later paper in which new identifications are made for some of these lines. The data are quite fragmentary in some cases, and in other cases rather doubtful, so that it has been thought better to make the evaluation of the constants for this state independently of the data obtained from the visible spectrum. It is hoped that the present work may lead to a more definite identification of some lines in the visible spectrum.

We now have complete data on the constants of the rotational energy functions for the  $1s^1\Sigma$ ,  $2p^1\Sigma$  and  $2p^1\Pi_{cd}$  states of the molecule. The values of the rotational function  $F$  for all observed vibrational and rotational states in these levels are given in Table VI.

The values of the rotational energy function given in Table VI allow the calculation of the origin of each band in the  $2p^1\Sigma - 1s^1\Sigma$  and  $2p^1\Pi_{cd} - 1s^1\Sigma$  systems from the value of the wave number of each line in the band under consideration, by means of the familiar relation:

$$\nu = \nu_0 + (F' - F'') \quad (24)$$

where  $\nu$  is the wave number of the line considered, and  $\nu_0$  is the origin of the band to which it belongs.

This calculation has been made for all the observed lines in the two systems above mentioned. The results of the calculation for the bands obtained in the present work are given in Table VII together with observed wave numbers of lines and eye estimates of their intensities. A few bands, the analysis of which is somewhat uncertain, are not included in the table. With the values of the origins of the bands as determined above, calculated values of the wave numbers of all identified lines are given. The agreement

<sup>25</sup> M. L. Chalk, Proc. Roy. Soc. A128, 579 (1930).

TABLE VI.

A. Value of  $F=B(K+\frac{1}{2})^2+D(K+\frac{1}{2})^4+F(K+\frac{1}{2})^6$  for  $1s^1\Sigma$  state.

$K$	0	1	2	3	4	5	6	7
$v=0$	14.84	133.31	369.19	720.30	1183.55	1754.94	2427.77	3202.82
1	14.10	126.68	350.80	684.36	1124.35	1666.92	2307.53	3041.12
2	13.38	120.22	332.88	649.34	1066.68	1581.18	2188.45	2883.65
3	12.67	133.86	315.24	614.86	1009.91	1496.77	2071.25	2728.68
4	11.96	107.49	297.57	580.34	953.05	1412.25	1953.88	2573.49
5	11.24	101.02	279.64	545.29	895.35	1326.46	1834.74	2415.93
6	10.52	94.49	261.54	509.91	837.07	1239.82	1714.42	2256.80
7	9.78	87.87	243.18	474.03	777.97	1151.94	1592.36	2095.31
8	9.02	81.04	224.24	437.00	716.98	1061.24	1466.37	1928.69
9	8.21	73.74	204.01	397.45	651.83	964.32	1331.68	1750.44
10	7.35	65.99	182.50	355.39	582.57	861.19	1188.33	1560.65
11	6.41	57.56	159.12	309.65	507.14	748.99	1032.31	1353.99
12	5.14	46.12	127.39	247.57	404.72	596.41	819.88	1072.23

B. Value of  $F=B(K+\frac{1}{2})^2+D(K+\frac{1}{2})^4+F(K+\frac{1}{2})^6$  for  $2p^1\Sigma$  state.

$v=0$	4.86	43.70	120.99	236.02	387.75	574.89	759.98	1049.52
1	4.62	41.52	114.99	224.42	368.94	547.47	758.84	1001.85
2	4.41	39.66	109.87	214.52	352.86	523.99	726.95	960.80
3	4.23	38.05	105.43	205.92	338.86	503.50	699.02	924.71
4	4.07	36.55	101.30	197.91	325.82	484.36	672.89	890.84
5	3.91	35.12	97.35	190.25	313.32	466.02	647.83	858.32
6	3.75	33.72	93.50	182.78	301.13	448.11	623.30	826.44
7	3.61	32.42	89.90	175.78	289.71	431.31	600.28	796.49

C. Value of  $F=B_d(K+\frac{1}{2})^2+D_d(K+\frac{1}{2})^4+F_d(K+\frac{1}{2})^6$  for  $2p^1\Pi_d$  state.

$v=0$	7.74	69.53	192.62	376.03	618.29	917.57	1271.64	1678.00
1	7.35	66.01	182.84	356.92	386.83	870.82	1206.75	1592.24
2	6.95	62.47	173.05	337.79	555.34	824.02	1141.80	1506.41
3	6.56	58.95	163.26	318.68	523.88	777.27	1076.91	1420.63
4	6.17	55.42	153.49	299.57	492.42	730.52	1012.01	1334.87

D. Value of  $F=B_c(K+\frac{1}{2})^2+D_c(K+\frac{1}{2})^4+F_c(K+\frac{1}{2})^6$  for  $2p^1\Pi_c$  state.

$v=0$	7.65	68.75	190.46	371.82	611.42	907.43	1257.69	1659.71
1	7.27	65.37	181.10	353.53	581.31	862.72	1195.66	1577.79
2	6.88	61.79	171.17	334.14	549.38	815.26	1129.80	1490.75
3	6.48	58.22	161.27	314.80	517.56	767.98	1064.18	1404.04
4	6.11	54.89	152.05	296.77	487.89	723.91	1003.04	1323.29

between the observed and calculated values of each line is the best evidence of the correctness of our calculated  $F$  values. In the case of the  $2p^1\Pi_{cd}-1s^1\Sigma$  bands, the origins are determined from the lines of the  $Q$  branches alone, since these are unperturbed, whereas a considerable number of perturbations appear in the levels associated with the  $P$  and  $R$  branch lines as shown by the table. Lines known to be blends are indicated in the table by an asterisk.

### Perturbations

It may be seen by examination of Table VII that the differences between observed and calculated wave numbers of lines in bands of the

$2p^1\Sigma-1s^1\Sigma$  system are in practically every case within the limits of experimental error (about  $2\text{ cm}^{-1}$ ). This is not so, however, for the lines of the  $2p^1\Pi_{cd}-1s^1\Sigma$  band system. But in every case these deviations of observed from calculated wave numbers may be explained by assuming a number of perturbations in the  $d$  levels of the  $2p^1\Pi_{cd}$  state. The  $c$  levels are all found to be regular, as shown by the very good agreement between calculated and observed wave numbers for all  $Q$  branch lines.

The most remarkable of the perturbations is found in the  $v=3$  level. Here the separation of all the  $c$  and  $d$  states averages  $10.4\text{ cm}^{-1}$  greater than the value calculated by assuming no perturbations to exist. This is evidenced by the fact that

TABLE VII. A. Bands of the  $2p^1\Sigma - 1s^1\Sigma$  system.

R branches				R branches				R branches				P branches								
K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	
3-0 band $\nu_0 = 94052.60$																				
1	2	94027.4	94024.7	0.0	0	3B	79772.8	79773.2	-0.4	1-3	band $\nu_0 = 79744.32$	79634.6	79635.1	-0.5	0	1	79744.8	79745.3	-0.5	
2	00B	93891.1	93889.3	-0.2	1	3	92636.3	92636.5	-0.2	1	3	79470.9	79470.9	0.0	1	2	79470.9	79470.9	0.0	
3	1	93671.5	93671.2	-0.3	2	1	92124.0	92126.3	-2.3	2	1	79653.4	79653.5	-0.1	2	3	79244.3	79244.5	-0.2	
4	0	93372.1	93372.5	-0.4	3	2	91545.2	91548.8	-3.6	3	3	79498.1	79498.4	-0.3	3	4	78959.6	78958.8	0.8	
5	1	92998.5	92996.7	1.8	4	0				4	3				4	3				
4-0 band $\nu_0 = 95264.98$																				
0	3	95288.6	95286.7	0.2	0	3	84688.7	84689.7	-1.0	5-3	band $\nu_0 = 84666.29$	84556.3*	84556.3	0.0	0	3	84688.7	84689.7	-1.0	
3	3	94869.7*	94870.5	-0.8	1	4	84650.4	84649.8	0.6	1	4	84650.4	84649.8	0.6	1	4	84386.9	84386.2	0.7	
4	0	94566.1	94565.8	0.3	2	2	84542.6	84541.4	1.2	2	4	84542.6	84541.4	1.2	2	4	84149.6	84148.8	0.8	
					4	2	84118.4	84122.4	-4.0	4	3	83847.8	83846.6	1.2	4	3	83847.8	83846.6	1.2	
					5	2	83835.5	83835.9	-0.4	5	3	83817.4	83817.4	0.0	5	3	83482.1	83482.8	-0.7	
					6	0	93319.3	93319.6	-0.3											
6-0 band $\nu_0 = 97592.84$																				
2	00	97406.8	97407.4	-0.6	0	1	85835.2	85834.2	1.0	6-3	band $\nu_0 = 85813.15$	85703.0	85703.0	0.0	0	1	85703.7	85703.0	0.7	
3	00	97174.2	97176.3	-2.1	1	4	85793.1	85792.8	0.3	1	3	85532.2	85531.6	0.6	1	3	85532.2	85531.6	0.6	
4	3	96865.5	96863.1	2.4	2	1	85680.7	85680.7	0.0	2	3	85292.6	85291.8	0.8	2	3	85292.6	85291.8	0.8	
5	3	96472.9	96471.8	1.1	3	2B	85500.3	84999.4	0.9	3	4B	84984.3	84986.1	-1.8	3	4	84984.3	84986.1	-1.8	
					4	0	95021.9	95023.9	-2.0	4	3	84955.9	84959.7	-3.8	4	3	84620.8	84617.5	3.3	
					7	3B														
3-1 band $\nu_0 = 89895.83$																				
0	0	89919.6	89919.7	-0.1	0	1	89773.2	89773.3	-0.1	0-4	band $\nu_0 = 74957.19$	74853.8	74854.6	-0.8	0	3	74900.5	74908.9	-8.4	
1	1	89873.9	89874.5	-0.6	1	0	89581.9	89583.0	-1.1	1	4	74970.7	74970.7	0.0	1	6	74972.1	74970.7	1.4	
2	1	89750.5	89750.9	-0.4	2	4B	89317.4	89316.9	0.5	2	1	74896.7	74895.6	1.1	2	4	74896.7	74895.6	1.1	
3	0	89589.7	89590.3	-0.6	3	4	88978.9	88977.4	1.5	3	0				3	7	74495.4	74497.8	-2.4	
4	1	89274.9	89274.9	0.0	4	3	88568.9	88567.7	1.2	4	3				4	5	74495.4	74497.8	-2.4	
					5	4				1-4	band $\nu_0 = 76278.63$	76176.7	76175.8	0.9	5	3	76222.5	76222.6	-0.1	
					6	1	93444.2	93449.8	-5.6	6	1	76307.5	76308.2	-0.7	6	2	76022.5	76022.6	-0.1	
1	2	93398.8	93397.3	1.5	2	3	93115.0	93113.2	1.8	2	2	76285.8	76286.1	-0.3	2	2	75813.8	75813.3	0.5	
2	2	93263.1	93263.2	-0.1	3	4	92841.4	92839.6	1.8	3	3	76204.5	76205.5	-1.0	3	3	75550.1	75550.0	0.1	
3	2	93049.1	93049.7	-0.6	4	3	92490.3	92489.6	0.7	4	2	76068.1	76067.2	0.9	4	0	75235.0	75235.3	-0.3	
					5	4	92066.3	92067.1	-0.8	5	2					5	1			
5-1 band $\nu_0 = 92284.56$																				
0	3	92304.5	92305.6	-1.1	0	1	93308.2	93307.3	0.9	2-4	band $\nu_0 = 77558.74$	77455.9	77455.7	0.2	0	1	77586.8	77586.4	0.4	
1	2	92255.2	92255.3	-0.1	1	3	93115.0	93113.2	1.8	1	4	77561.4	77565.7	-4.3	1	4	77301.6	77300.8	0.8	
2	2	92124.0	92124.0	0.0	2	3	92841.4	92839.6	1.8	2	2	77475.6	77475.7	-0.1	2	2	77088.7	77088.3	0.4	
3	2	91913.4	91913.6	-0.2	3	4	92490.3	92489.6	0.7	3	00	77331.1	77331.3	-0.2	3	5	76821.9?	76819.2	2.7	
4	00	91627.0	91626.3	0.7	4	4	92066.3	92067.1	-0.8	4	3				4	1	76497.3	76499.4	-2.1	
					5	3B				3-4	band $\nu_0 = 78804.51$	78830.6	78830.6	0.0	5	3	76497.3	76499.4	-2.1	
1-2 band $\nu_0 = 83440.01$																				
0	2	82467.7	82468.2	-0.5	0	1B	78830.1	78830.6	-0.5	3-4	band $\nu_0 = 80016.05$	80040.6	80040.6	0.0	0	3B	80039.4	80040.6	-1.2	
1	2	82335.1	82334.8	0.3	1	3	92161.2	92161.8	-0.6	1	4	80011.0	80009.9	1.1	1	4	79756.1	79755.0	1.1	
2	2	82255.2	82255.3	-0.1	2	3	91969.0	91968.9	0.1	2	4	80011.0	80009.9	1.1	2	1	79756.1	79755.0	1.1	
3	2	82124.0	82124.0	0.0	3	4	91698.1	91697.6	0.5	3	2	79916.4	79916.4	0.0	3	4	79537.9	79537.0	0.9	
4	00	81913.4	81913.6	-0.2	4	5	91349.1	91350.5	-1.4	4	3	79762.9	79761.5	1.4	4	4B	79258.0	79260.9	-2.9	
					5	3B	90932.9	90931.0	1.9	5	0B	82224.5	82227.8	-3.3	5	0				
					6	0B	82224.5	82227.8	-3.3	6	3					1	1B	81186.2	81186.2	0.0
2-2 band $\nu_0 = 84720.77$																				
0	2	84748.5	84747.1	1.4	0	3	84606.4	84605.0	1.4	7-4	band $\nu_0 = 83460.92$	83481.4	83481.4	0.0	0	3	83482.1	83481.4	0.7	
1	5	84708.9*	84710.9	-2.0	1	4	84429.2	84427.6	1.6	1	2	83443.3	83443.3	0.0	1	2	83443.3	83443.3	0.0	
2	4	84606.4*	84604.1	2.3	2	3	84183.4	84181.8	1.6	2	3B	83359.1	83359.1	0.0	2	3	83359.1	83359.1	0.0	
3	4	84425.7*	84428.9	-3.2	3	5	83870.3	83870.3	0.0	3	2B	83170.3	83170.3	0.0	3	4	82971.4	82970.5	0.9	
					4	3	83494.0	83497.0	-3.0	4	0					4	0	82684.7	82683.7	1.0
0-3 band $\nu_0 = 78426.57$																				
0	3	78455.6	78457.6	-2.0	0	2	75591.4	75589.5	1.9	3-5	band $\nu_0 = 75562.73$	75589.5	75589.5	0.0	0	2	75591.4	75589.5	1.9	
1	3	78433.6	78433.7	-0.1	1	3	78317.1	78317.6	-0.5	1	4	75567.1	75567.1	0.0	1	4	75567.1	75567.1	0.0	
2	1B	78347.2	78347.4	-0.2	2	3	78155.0	78155.0	0.0	2	3	75489.0	75489.0	0.0	2	3	75489.0	75489.0	0.0	
3	4	78199.5	78199.5	0.0	3	6	77932.3	77932.7	-0.4	3	3	75357.0	75356.3	0.7	3	4	75123.6	75122.0	1.6	
4	0	77992.8	77991.6	1.2	4	4	77653.7	77652.7	1.0	4	00	75170.9	75170.9	0.0	4	3B	74870.0	74873.3	-3.3	
					5	4	77319.6	77317.6	2.0	5	00	74933.1	74933.3	-0.2	5	2	74572.5	74575.1	-2.6	

TABLE VII, A. Bands of the  $2p^1\Sigma - 1s^1\Sigma$  system. (Continued.)

R branches				P branches				R branches				P branches							
K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C
5-5 band $\nu_0 = 77956.61$																			
0	2	77980.2	77980.5	-0.3	0	2	79125.3	79124.9	0.4	6-5 band $\nu_0 = 79102.37$									
1	4B	77953.1	77952.9	0.2	1	4	77859.2	77859.5	-0.3	0	4	79095.7	79094.9	0.8	1	5	79005.6*	79005.1	0.5
2	4	77866.1	77867.2	-1.1	2	5	77508.4	77508.7	-0.3	1	4	79005.6*	79005.5	0.1	2	4	78857.7*	78856.5	1.2
3	4	77724.8	77724.6	0.5	3	3	77252.5	77251.5	1.0	2	5	79005.6*	78858.2	-0.5	3	5	78651.0	78650.9	0.1
					4	4	76944.6*	76943.5	1.1	3	4	78857.7*			4	4	78386.7	78389.8	-3.1
					5	3													

TABLE VII, B. Bands of the  $2p^1\Pi_{cd} - 1s^1\Sigma$  system.

Band	$\nu_0$	Branch	K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	Band	$\nu_0$	Branch	K''	I	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	
0-2	91002.24	R	0	4	91058.6	91058.4	0.2			P	2	3	89370.0	89368.7	1.3	
			1	4	91075.7	91074.6	0.9				3	4	89184.5	89185.9	-1.4	
			2	3	91044.2	91045.4	-1.2				4	4	88964.8	88964.9	-0.1	
			3	4	90973.4*	90971.2	2.3				5	2	88708.0	88709.9	-1.9	
		P	2	4	90739.2	90738.9	0.3			Q	2	6	89569.8	89569.4	0.4	
			3	5	90547.5	90545.5	2.0				5	5	89483.8	89483.8	0.0	
			4	4	90311.4	90311.6	-0.2				5	5	89356.5*	89366.6	-0.7	
		Q	4	4	90044.2	90039.4	4.8				5	3	89188.6	89189.3	-0.4	
			7	7	90950.7	90950.8	-0.1				5	3	88978.9*	88983.9	0.4	
			4	5	90859.8	90859.8	-0.0				5	5	86202.1	86201.5	0.6	
			3	5	90724.3	90724.7	-0.4				5	6	86224.9	86224.9	0.0	
			4	5	90547.5	90547.0	0.5				5	6	86224.9	86224.9	0.0	
			5	5							5	6	86153.9	86152.9	1.0	
0-3	87308.89	R	0	3	87366.2*	87365.8	0.4			P	2	3	86068.9	86068.9	0.0	
			1	7	87388.7	87387.7	1.0				3	4	85974.8	85974.8	0.0	
			2	1	87372.4	87369.7	2.7				4	4	85915.8	85915.8	0.0	
			3	4	87315.6	87312.3	3.3				4	4	85741.8	85741.8	0.0	
			4	0	87218.9	87216.6	2.3				4	4	85554.7*	85554.7	0.0	
		P	3	5	87065.0	87063.2	1.8				5	0	85318.1	85321.0	-2.9	
			3	5	86888.0	86886.7	1.3				5	0	85108.4	85108.4	0.0	
			5	3	86676.1	86675.0	1.1				5	5	86100.7	86105.3	-4.6	
			3	3	86433.3	86430.4	2.9				5	5	86031.8	86030.9	0.9	
		Q	1	5	87263.8	87263.8	0.0				5	2	85920.2	85920.6	-0.4	
			2	5	87185.4	87184.1	1.3				5	2	85776.2	85776.2	0.0	
			3	5	87065.0	87065.9	-0.9				5	2	85597.3	85597.9	-0.6	
			4	3B	86910.3	86910.4	-0.1				5	1	85388.0	85389.2	-1.2	
			5	3	86719.2	86719.6	-0.4				5	1	85388.0	85389.2	-1.2	
0-4	838401.02	R	1	4	83927.5*	83926.2	1.3			R	0	3B	82961.9	82961.1	0.8	
			2	4B	83915.9	83919.5	-3.6				1	6B	82989.7	82988.1	1.6	
			3	2	83851.0	83879.0	-2.9				2	3B	82984.2	82983.6	0.6	
		P	2	1	83612.7	83613.0	-0.3				2	3B	82947.5*	82947.8	-0.3	
			3	3	83454.3	83453.5	0.8				2	3B	82883.2	82881.8	1.4	
			4	0	83258.3	83204.0	54.3				2	3B	82694.2	82692.7	1.5	
			5	0	83002.2	83047.1	-44.9				3	3	82541.6*	82543.9	-2.3	
		Q	1	4	82802.2	82807.1	-4.9				3	3	82370.3*	82367.9	2.4	
			2	4	82733.6	82733.6	0.0				4	5	82160.5	82166.7	-6.2	
			3	4	82633.6	82633.6	0.0				4	4B	82111.1	82107.7	3.4	
			4	4	82494.0	82494.0	0.0				5	5	82806.9	82807.8	-0.9	
			5	2	83337.5*	83336.2	1.3				5	3	82714.3	82714.3	0.0	
1-1	97239.72	P	1	4B	97298.3	97295.9	2.4			R	0	3B	82590.9	82592.3	-1.4	
			2	6	96957.1	96954.9	2.2				0	6B	95532.6	95532.6	0.0	
			3	6	96739.6	96738.2	1.4				0	6B	95536.2	95536.2	0.0	
			4	3	96472.9	96472.3	0.6				2	4B	95487.8	95481.5	6.3	
			5	7B	96157.0*	96159.6	-2.6				3	0	95396.4	95389.3	7.1	
			6	4	96070.0	96070.0	0.0				4	4	95214.0	95212.9	1.1	
		Q	2	3	96009.0	96008.9	0.1				5	5	95007.5	95007.0	0.5	
			3	5	96696.6	96696.7	-0.1				5	5	94747.2	94754.3	-7.1	
			4	4	96438.3	96435.5	2.8				5	0B	94464.2	94457.3	6.9	
			5	1	96337.5*	96336.2	1.3				5	5	95425.4	95424.9	0.5	
1-3	89617.92	R	0	6	89671.6	89671.3	0.3				1	5	95322.5	95321.6	0.9	
			1	7	89687.6	89686.9	0.7				2	4	95168.3	95168.1	0.2	
			2	4	89661.0	89659.6	1.4				3	5	94965.3	94966.0	-0.7	
			3	3B	89589.3	89589.9	-0.6				4	1	94716.6	94717.4	-0.8	
			4	2	89479.1	89478.9	0.2				5	5	91839.8	91839.8	0.0	
												4	4	91849.2	91849.2	0.0
												2	2	91804.4	91804.4	0.0
												3	3	91730.5	91730.5	0.0



TABLE VII. B. Bands of the  $2p^1\Pi_{cd} - 1s^2\Sigma$  system. (Continued.)

Band	$\nu_0$	Branch	$K''$	$I$	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C	Band	$\nu_0$	Branch	$K''$	$I$	Obs.cm <sup>-1</sup>	Calc.cm <sup>-1</sup>	O-C
2-4	88324.97	R	0	2	88377.0	88375.5	1.5	3-6	84111.22	R	1	6	84191.2	84180.0	11.2
			1	5	88391.1	88390.5	0.6				2	4	84178.3	84168.4	9.9
			2	1	88358.7	88365.2	-6.5				3	3	84135.6	84103.3	32.3
			3	0	88309.2	88300.0	9.2				4B	2	83753.9†	83708.0	45.9
			3B	2	88091.1	88089.9	1.2				5	1	83705.0	83592.6	112.4
			4	3	87917.2	87917.7	-0.5				2	2	83601.9	83592.6	9.3
			4	1	87702.7	87709.7	-7.0				2	2	83407.4	83392.8	14.6
			4	3	88280.5	88279.5	1.0				4	4	84075.2	84075.3	-0.1
			4	4	88199.4	88199.1	0.3				4B	2	84011.0	84011.0	0.0
			5	3	88078.7	88079.8	-1.1				1	1	83915.6	83915.6	0.0
2-5	85080.05	R	0	4	87731.4	87730.5	0.9	3-7	81327.89	R	0	2	81388.5	81377.1	11.4
			1	5	85133.0	85132.5	0.5				1	5	81414.2*	81403.3	10.9
			1	5B	85153.9	85153.3	0.6				2	5	81414.2*	81403.3	10.9
			2	4	85133.0	85139.4	-6.4				3	3	81388.5	81377.8	10.7
			3	3	85101.5	85091.3	10.2				4	4	81337.0	81327.2	9.8
			4	4	84864.7	84864.1	0.6				1B	2	81337.0	81327.2	9.8
			4	4	84708.9	84709.0	-0.1				5	5	81155.8	81143.7	12.1
			5	0	84516.9	84523.7	-6.8				1	1	81028.1	81017.1	11.0
			5	0	84316.5	84310.1	6.4				3	3	80879.3	80868.6	10.7
			5	2	85042.5	85042.0	0.5				3	3	80711.3	80699.8	11.5
2-6	82067.48	R	0	4	82170.7*	82169.4	1.3	4-5	89042.67	R	0	2B	89087.3	89086.0	1.3
			1	5B	82145.8*	82146.0	-0.2				1	2B	89009.2	89004.5	4.7
			2	4	82145.8*	82142.2	3.6				2	2B	88818.9	88817.6	1.3
			3	4	82170.7*	82110.0	60.7				3	3	88554.1	88650.0	-95.9
			4	2	81869.4	81868.4	1.0				4	4	88554.1	88554.1	0.0
			4	2	81730.4	81730.6	-0.2				4	4	88996.1	88995.7	0.4
			5	2	81560.5	81568.7	-8.2				1	1	88914.3	88914.2	0.1
			5	2	81388.5	81383.0	5.5				3	3	88792.8	88793.3	-0.5
			5	2	82035.7	82034.8	0.9				4	4	88629.1	88634.4	-5.3
			5	4	81978.2	81977.1	1.1				1B	2	88438.7	88439.3	-0.6
3-4	90368.38	R	0	2	90424.7	90415.4	9.3	4-7	83240.68	R	0	1	83289.5†	83286.3	3.2
			1	3	90433.4	90424.2	9.2				1	2	83311.3	83306.3	5.0
			2	1	90398.2	90389.5	8.7				2	1	83295.5	83297.1	-1.6
			3	0	90141.8	90129.8	12.0				3	0	83258.3	83259.1	-0.8
			3	4	89961.7	89951.3	10.4				3	2	83050.2	83052.9	-2.7
			4	2	89744.7	89734.0	10.7				4	2	82926.1	82920.2	5.9
			4	2	89471.5	89480.0	-8.5				0	0	82764.7	82762.3	2.4
			5	2	89471.5	89471.5	0.0				4	4	83208.2	83207.7	0.5
			5	2	90316.3	90319.1	-2.8				6B	2	83148.2	83149.6	-1.4
			5	4	90231.5	90232.1	-0.6				4B	2	83064.5	83063.4	1.1
3-4	90368.38	P	0	2	90102.8	90102.8	0.0	4-8	80699.29	R	0	3	80747.1	80745.2	1.9
			1	4	89933.3	89932.9	0.4				1	6	80774.9*	80771.2	3.7
			2	1	89724.3	89724.1	0.2				2	5	80774.9*	80774.1	0.8
			3	4	89724.3	89724.1	0.2				3	2	80531.8	80529.9	1.9
			4	1	89724.3	89724.1	0.2				4	5	80419.9	80415.3	4.6
			5	1	89724.3	89724.1	0.2				5	1	80287.8	80281.3	6.5
			5	2	89724.3	89724.1	0.2				4	1	80128.1	80129.9	-1.8
			5	2	89724.3	89724.1	0.2				5	5	80672.3	80672.6	-0.3
			5	4	89724.3	89724.1	0.2				1	7	80626.9	80626.6	0.3
			5	4	89724.3	89724.1	0.2				2	4	80558.1	80558.5	-0.4
5	5	89724.3	89724.1	0.2	3	4	80469.9	80469.7	0.2						

every line in the  $P$  and  $R$  branches of bands originating on this level gives a value of  $\nu_0$   $10.4 \text{ cm}^{-1}$  (to within the experimental error) greater than the  $\nu_0$  given by lines of the  $Q$  branches. Since all the other perturbations in the band system are found in the  $d$  states, and since, as has been remarked previously, the  $B_c^x$  values, in contradistinction to the  $B_d^x$  values, when given as a function of  $v$ , fall regularly on a smooth curve, it may be assumed that the perturbations exist entirely in the  $d$  state. This, then, seems to be a vibrational perturbation, all of the  $d$  rotational levels of the  $v=3$  state being shifted by  $10.4 \text{ cm}^{-1}$ .

In the other vibrational states of the  $2p^1\Pi_d$  level, most of the rotational levels are either not perturbed or have perturbations scarcely greater than the errors of measurement. There are, however, as is apparent at once from Table VII, a number of rather large perturbations. These perturbed levels, together with the amount of the perturbation in  $\text{cm}^{-1}$  units, are given in Table VIII. A plus perturbation means an increase in the energy of the state.

TABLE VIII. Perturbations in rotation levels of  $2p^1\Pi_d$  state.

$v$	$K=1$	2	3	4	5
0				3.2	
1					
2			-7.4	7.3	
3	10.5	10.5	10.1	10.6	9.8
4		4.5			

The properties of the  $2p^1\Sigma$  and  $2p^1\Pi_{cd}$  levels of  $\text{H}_2^{26}$  are given in the diagram of Fig. 4. It may be seen that all of the  $2p^1\Sigma$  levels and the  $d$  levels of the  $2p^1\Pi_{cd}$  state satisfy all the conditions, as given by Dieke,<sup>27</sup> necessary that two different levels may perturb each other. It is therefore quite probable that these two sets of levels are perturbing one another. Unfortunately this cannot be directly verified. The overlapping of the levels of the two states begins at the vibrational level  $v=7$  of the  $2p^1\Sigma$  state. Schaafsma and Dieke's<sup>6</sup> and Hyman's<sup>7</sup> analyses include a few bands having the initial states  $v'=8$  and  $v'=9$ , but none of these bands yield consistent values of

<sup>26</sup> See R. S. Mulliken, Rev. Mod. Phys. 3, 149 (1931) and 4, 78 (1932).

<sup>27</sup> G. H. Dieke, Phys. Rev. 38, 646 (1931).

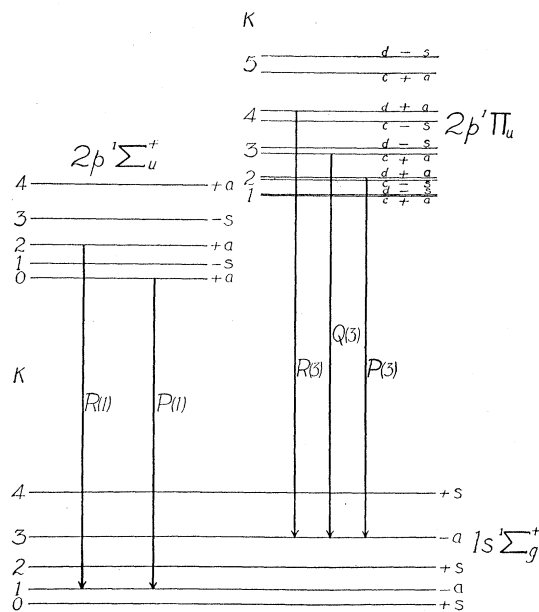


FIG. 4. Schematic energy level diagram showing properties of the states.

$\Delta_2 F'$ . It has therefore been impossible to calculate values of the molecular constants for these states. It is thought that some of the lines listed by the above authors have been given incorrect quantum assignments. On the other hand many of these levels may have perturbations and some of the  $\Delta_2 F'$  values may, for that reason, deviate from a smooth curve. Richardson has found no bands ending on the  $2p^1\Sigma$  state, in the visible spectrum, for which  $v$  is greater than 7. It should be remembered that in  $^1\Sigma-^1\Sigma$  bands there occur only  $P$  and  $R$  branches, perturbations of both of which may show. Hence it is quite difficult to effect an analysis in case there should be a large number of such perturbations. It is significant that no perturbations are found in the  $2p^1\Sigma-1s^1\Sigma$  bands for any values of  $v$  less than 7. Several different lines of evidence thus point to the conclusion that the two states in question do perturb each other.

#### The vibrational and electronic levels

The values of the origins of the bands given in Table VII enable us to obtain the vibrational term differences (denoted by  $\Delta G$ ) for all the observed levels of the three electronic states considered in this investigation. Since the

TABLE IX.  $\Delta G$  values ( $\text{cm}^{-1}$ ).

State	$1s^1\Sigma$		$2p^1\Sigma$ Ultra- violet	Richardson	$2p^1\Pi_{cd}$
$v$	$\Delta$				
$\frac{1}{2}$	4161.70	238.80	1318.85	1318.586	2309.38
$1\frac{1}{2}$	3922.90	228.37	1281.72	1281.676	2171.39
$2\frac{1}{2}$	3694.53	226.01	1246.38	1246.715	2044.01
$3\frac{1}{2}$	3468.52	228.30	1213.56	1213.184	1914.17
$4\frac{1}{2}$	3240.22	225.54	1180.03	1180.102	
$5\frac{1}{2}$	3014.68	231.93	1147.86	1147.645	
$6\frac{1}{2}$	2782.75	238.62	1115.59	1115.642	
$7\frac{1}{2}$	2544.13	250.77			
$8\frac{1}{2}$	2293.36	266.20			
$9\frac{1}{2}$	2027.16	288.65			
$10\frac{1}{2}$	1738.51	320.47			
$11\frac{1}{2}$	1418.04				

spectrograph used in the present work did not permit us to photograph the longer wave-length bands of the  $2p^1\Sigma - 1s^1\Sigma$  system our own data have been supplemented by that of Hyman,<sup>7</sup> in determining  $\Delta G$  values for the  $2p^1\Sigma$  and  $1s^1\Sigma$  states. The resulting values of  $\Delta G$  for the three states are given in Table IX. The values for the  $2p^1\Sigma$  state as determined from the extreme ultraviolet spectrum are compared, in the table, with those given by Richardson and Davidson<sup>19</sup> in their analysis of the bands in the visible spectrum and are seen to agree well within the limits of experimental error. In obtaining Table IX all possible independent combinations of the  $\nu_0$  values were used so as to obtain the best average values of  $\Delta G$ .

It may be mentioned again that, due to the scarcity of standard lines in the extreme ultraviolet, the relative values of wave-lengths over large intervals may have considerably larger probable errors than do relative wave-lengths within small intervals. It may be seen that the values of  $\Delta G$  given in Table IX are of the order of ten times the  $\Delta_2 F$  values that are used in determining the rotational constants. The probable error in  $\text{cm}^{-1}$  units of any  $\Delta G$  value is therefore larger than the probable error of the  $\Delta_2 F$  values given previously. It is thought,

however, that the probable error in any value of  $\Delta G$  given in Table IX is in all probability smaller than  $2 \text{ cm}^{-1}$ . The agreement of the values obtained for the  $2p^1\Sigma$  state with those of Richardson and Davidson indicate a definitely smaller probable error than this.

Since the probable error of Rasetti's Raman effect measurements<sup>16</sup> is less than that for the measurements in the extreme ultraviolet, the value of  $\Delta G_1$  given in Table IX for the  $1s^1\Sigma$  state is that determined from his data.<sup>16</sup> The value determined in the present investigation is  $\Delta G_1 = 4160.83 \text{ cm}^{-1}$ , which differs by less than  $1 \text{ cm}^{-1}$  from the Raman effect value. This furnishes a check upon the validity of the Raman effect work and entirely substantiates it.

In Table IX are given also the first differences of the  $\Delta G$  values for the  $1s^1\Sigma$  state. It may be seen from these differences, as well as from Fig. 5, that

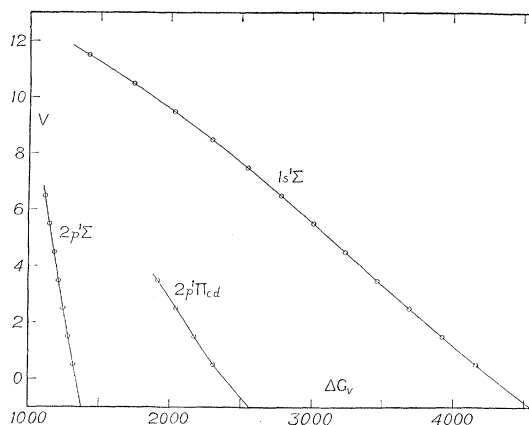


FIG. 5.  $\Delta G_v : v$  plot for the  $1s^1\Sigma$  (A),  $2p^1\Sigma$  (B) and  $2p^1\Pi_{cd}$  (C) states.

the  $\Delta G : v$  function has a very pronounced positive curvature at the value  $v = \frac{1}{2}$ . The more fragmentary data available previous to the present work<sup>16</sup> had indicated a large deviation of the value of  $\Delta G_1$  from a  $\Delta G : v$  curve which was then assumed to be linear for low values of  $v$ . This deviation was at the time of the former work ascribed to a vibrational perturbation. The present data indicate, however, that it is unnecessary to assume such a perturbation.

A least squares equation giving  $\Delta G_v$  as a function of  $v$  designed to fit the data from  $v = -\frac{1}{2}$  to  $v = 5\frac{1}{2}$  is:

$$\Delta G_v = 4417.19 - 262.63(v + \frac{1}{2}) + 9.34619(v + \frac{1}{2})^2 - 0.76(v + \frac{1}{2})^3 \quad (25)$$

but the extreme positive curvature of the function for small  $v$  does not allow an entirely satisfactory fitting of any equation of this type. The greatest difference between observed and calculated values of  $\Delta G$  when using the above equation is  $2.47 \text{ cm}^{-1}$ , which is somewhat larger than the probable error in any particular value of  $\Delta G_v$ .

The extrapolated value of  $\Delta G_e = 4417. \text{ cm}^{-1}$  was obtained by a graphical treatment in combination with difference tables.

The  $\Delta G : v$  form of the curve for the  $2p^1\Sigma$  state has been discussed by Birge.<sup>28</sup> A least squares equation representing the  $\Delta G_v : v$  function for this state is:

$$\Delta G_v = 1357.302 - 39.9307(v + \frac{1}{2}) + 1.218487(v + \frac{1}{2})^2 - 0.0638888(v + \frac{1}{2})^3. \quad (26)$$

The value of  $\Delta G_e = 1357.302 \text{ cm}^{-1}$  obtained from the above equation agrees sufficiently well for practical purposes with the value  $1358.33$  which was determined by use of difference tables. It should be noted that although the difference between observed and calculated values of  $\Delta G_v$  when using the above equation is in all cases less than  $0.3 \text{ cm}^{-1}$ , a cubic equation of the type derived is not capable of representing the data to within the experimental error. A graph of  $\Delta G_v : v$  for this state is given in Fig. 5.

For the  $2p^1\Pi_{ca}$  state  $\Delta G_v : v$  is shown graphically in Fig. 5 and a least squares representation is given by the equation:

$$\Delta G_v = 2471.05 - 177.867(v + \frac{1}{2}) + 18.375(v + \frac{1}{2})^2 - 2.17833(v + \frac{1}{2})^3. \quad (27)$$

It is thought that the value  $\Delta G_e = 2468 \text{ cm}^{-1}$  obtained by a semi-graphical treatment of the data, is more trustworthy than the extrapolated value  $2471$  given by the above equation.

The vibrational term value,  $G_v$ , may be obtained by integrating Eqs. (25), (26) and (27) from  $v = -\frac{1}{2}$  to  $v = v$ , or more accurately by

$$G_v = G_0 + \sum_{\frac{1}{2}}^{v-\frac{1}{2}} \Delta G_v = G_0 + G_v^* \quad (28)$$

by using for  $\Delta G_v$  the values listed in Table IX.  $G_0$  represents the vibrational term  $v=0$ , using the true electronic level  $v = -\frac{1}{2}$  as origin. Investigators often use  $v=0$  as origin, and we write the vibrational term value based on this origin as  $G_v^*$  in order to distinguish it from the true vibrational term value  $G_v$ . The value of  $G_0$  is given to a very close approximation by  $\frac{1}{2}\Delta G_{-1/4}$ , where  $\Delta G_{-1/4}$  is to be taken from Eqs. (25), (26) and (27). The results are  $2176.1$ ,  $673.7$  and  $1213.9 \text{ cm}^{-1}$ , respectively. The only remaining data necessary for the calculation of any spectral line are the electronic term values,  $T_e$ . But these are merely the origins of the two band systems,  $\nu_e$ , since by definition  $T_e = 0$  for the normal state. To obtain  $\nu_e$  we first calculate  $\nu_{00}$ , the origin of the  $0-0$  band. This is given by

$$\nu_{00} = \nu_0 - [G_v^{*'} - G_v^{*''}]. \quad (29)$$

Each band origin  $\nu_0$  as given in Table VII, used in conjunction with the values of  $G_v^*$  obtainable from Table IX, thus gives a value of  $\nu_{00}$ . The various values thus obtained were found to agree well within the limits of error and accordingly the arithmetic average was adopted as the most probable value. The results are  $90,206.1 \text{ cm}^{-1}$  for the  $2p^1\Sigma - 1s^1\Sigma$  system and  $99,087.4 \text{ cm}^{-1}$  for the  $2p^1\Pi_{ca} - 1s^1\Sigma$  system.

The true origin of each system is then given by

$$\nu_e = \nu_{00} - [G_0' - G_0''] \quad (30)$$

and the numerical results are  $91,708$  and  $100,049 \text{ cm}^{-1}$ , respectively.

The wave number of any line may now be obtained from the general equation

$$\nu = \nu_e + G_v' - G_v'' + F'(v, K) - F''(v, K). \quad (31)$$

The values of  $F'$  and  $F''$  are given in Table VI and the values of  $G_v'$  and  $G_v''$  are obtained from the quantities already used in Eq. (28). It is however simpler in practice to use the relation

$$\nu = \nu_{00} + G_v^{*'} - G_v^{*''} + F' - F''. \quad (32)$$

In conclusion attention may again be called to the fact that, in order to get a fairer estimate of the accuracy of the rotational functions  $F'$  and  $F''$ , the calculated values of  $\nu$  listed in Table VII were obtained from the simpler Eq. (24).

<sup>28</sup> R. T. Birge, Trans. Faraday Soc. 25, 707 (1929).

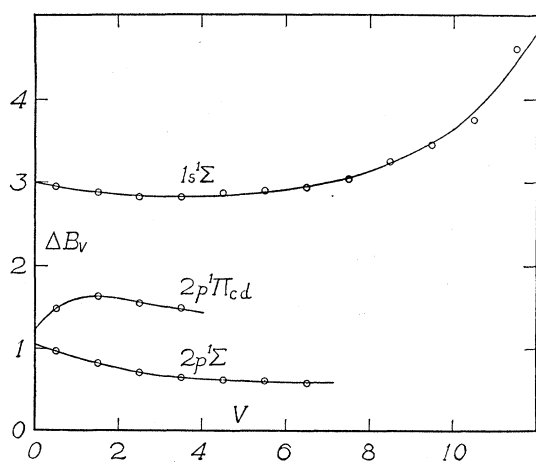
### Summary

The constants for the three electronic levels considered in this investigation are collected in Table X.

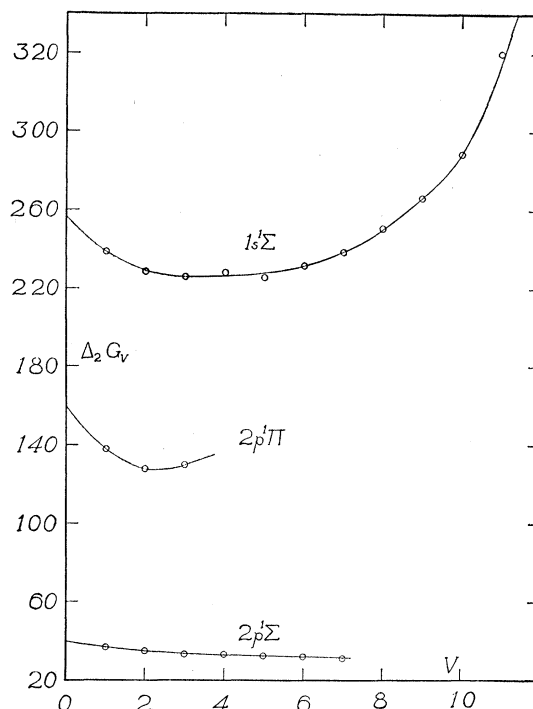
TABLE X.

	$1s^1\Sigma$	$2p^1\Sigma$	$2p^1\Pi_{cd}$
$T_e$ (cm <sup>-1</sup> )	0	91708	100,049
$G_0$ (cm <sup>-1</sup> )	2176.1	673.7	1213.9
$\Delta G_0[\omega_e]$ (cm <sup>-1</sup> )	4417.9	1358.33	2468
$2x_e\omega_e$ (cm <sup>-1</sup> )	262.63	39.931	177.867
$B_0$ (cm <sup>-1</sup> )	60.8715	19.987	31.288
$B_0$ (cm <sup>-1</sup> )	59.354	19.457	30.602
$D_e$ (cm <sup>-1</sup> )	-0.04652	-0.017188	0.020959
$F_e$ (cm <sup>-1</sup> )	$5.1806 \times 10^{-5}$	$2.9160 \times 10^{-5}$	$1.8901 \times 10^{-5}$
$I_e$ (g cm <sup>2</sup> )	$0.45437 \times 10^{-40}$	$1.38381 \times 10^{-40}$	$0.88399 \times 10^{-40}$
$r_e$ (cm)	$0.73949 \times 10^{-8}$	$1.2905 \times 10^{-8}$	$1.03145 \times 10^{-8}$
$\alpha_e$ (cm <sup>-1</sup> )	3.06709	1.19556	1.31673
$\nu_{00}$	$2p^1\Sigma - 1s^1\Sigma$ 90206.1	$2p^1\Pi_{cd} - 1s^1\Sigma$ 99087.4	

The data of the present investigation seem to indicate conclusively that in the normal state of the H<sub>2</sub> molecule the  $B_v : v$  and  $\Delta G_v : v$  curves have a quite unmistakable positive curvature for low values of  $v$ , changing to a negative curvature for higher values. Until recently, no such phenomenon had been observed in the case of the normal state of any molecule. Professor Birge has, however, found evidence<sup>29</sup> for just such a situation in the case of the oxygen molecule. This situation would seem to lead to the belief that the deviations from straight lines in the

FIG. 6.  $\Delta B_v : v$  plot for each of the three states.

<sup>29</sup> R. T. Birge, private communication.

FIG. 7.  $\Delta_2 G_v : v$  plot for each of the three states.

values of the above functions are not due to perturbations as was formerly supposed.

On the other hand there are a number of cases in which the  $B_v : v$  and  $\Delta G : v$  curves for excited states have initial positive curvature. An example of this is the  $2p^1\Sigma$  state investigated here. (See Figs. 3 and 5.) In the case of the  $2p^1\Pi_{cd}$  state the  $\Delta G_v : v$  function also has a positive initial curvature, but the  $B_v : v$  curve for the  $c$  component levels has for low values of  $v$  a negative curvature. (See Figs. 3 and 5.) The nature of the  $B_v : v$  and  $\Delta G_v : v$  functions is shown very well by curves of  $\Delta B_v : v$  and  $\Delta_2 G_v : v$  as given in Figs. 6 and 7. These curves also serve to show graphically the accuracy with which the experimental values of  $B_v$  and  $\Delta G_v$  fit smooth  $B_v : v$  and  $\Delta G_v : v$  curves.

In conclusion, the writer wishes to express his deep appreciation of the many valuable suggestions and the assistance that Professor Birge has so willingly given throughout the course of the investigation.

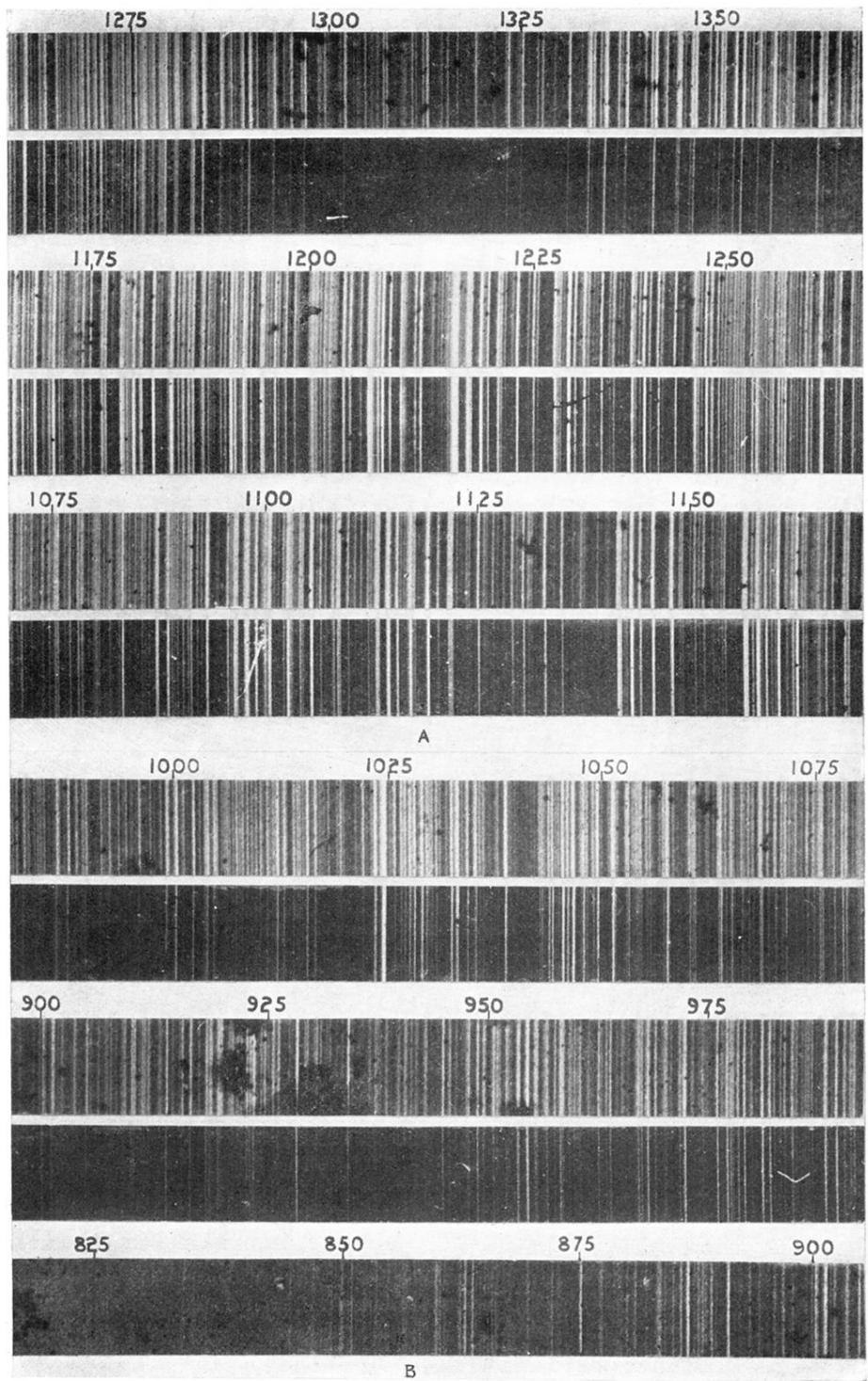


FIG. 2. Enlargements (about 4X) of two spectrograms. Exposure times 45 and 25 minutes, respectively.