

THE BANDS OF CH AND CN IN STELLAR SPECTRA

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ABSTRACT

The upper limit of visibility in the spectral sequence of the CH band at $\lambda 4300$ is found to be F8 (temperature about 6500°K). This value is considerably lower than has been adopted heretofore (classes F2 to A0; temperatures 7900° to 13000°K). The region occupied by the CH band is very rich in strong atomic lines and it is therefore not permissible to consider the general aspect of the Fraunhofer "G-band": the total intensity of the atomic lines greatly exceeds that of the molecular lines. The limit of visibility of the CN band at $\lambda 4200$ is found to be at F8, in agreement with former estimates. The simultaneous disappearance of CH and CN, having heats of dissociation of 110 and 210 k cal/mol respectively, may be explained by the great abundance of H in stellar atmospheres.

1. CONSIDERABLE progress has been made, in recent years, in the application of the theory of ionization equilibria to the problem of line-intensities in various types of stellar spectra. Most of the work done thus far has dealt with lines of atomic origin. There exists, however, a similar problem in the case of molecular spectra. In principle, the changes in intensity of a molecular absorption band could be investigated by using the same general method that has proved to be of such value in the interpretation of atomic spectra. But in actual practice the molecular problem is far more complicated than that of the atomic lines: not only is it necessary to introduce into the equations the partial pressures of the various constituents, but, in addition to this, the constituent atoms may give rise to several different molecular combinations. Furthermore, since the energy of a molecule is the sum of three terms, *viz.*, its electronic energy, the vibrational energy of the nuclei and the energy of rotation of the whole system, the number of energy levels of a molecule greatly exceeds that of an atom.

Several investigators have discussed the intensity of the bands of CH and CN as function of spectral class. The band $\lambda 4315$ of CH is observed in both branches of the spectral sequence: G—M and G—N. According to Rufus,² it reaches maximum intensity at R0 and at K0, respectively. Shane³ placed the maximum of sequence G—N in class R3. Beginning at N3 and at Mb the band is very faint. For the bands of cyanogen Lindblad⁴ found a maximum between G5 and K5, and Shane found another maximum near R5 in the secondary sequence G—N.

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² W. C. Rufus, Publications of the Observatory, University of Michigan, 3, 258 (1923).

³ C. D. Shane, Lick Observatory Bulletins 10, 79 (1919).

⁴ B. Lindblad, Astrophys. J. 55, 85 (1922).

With respect to the upper limits of temperature (or spectral class) at which the bands of CH and CN are at the limit of visibility, various estimates have been made, some of which are contradictory. In the case of CN the upper limit is usually⁵ placed between F5 and G0; however, several investigators⁶ believed that the band could be traced as far as A0. It seems certain that in stars of early spectral class the band near $\lambda 4200$ is of instrumental origin, being caused by absorption in the glass of the optical train.⁷ For the CH band a number of contradictory estimates have been made: some investigators⁸ place the upper limit at A0; others⁹ place it at F2.

It is generally believed¹⁰ that the CH band persists at considerably higher temperatures than the CN band. If this were correct it would lead to difficulties, since the heat of dissociation of CH is appreciably less than that of CN.

We have undertaken a careful redetermination of the limiting temperatures and have found that the values heretofore adopted for CH are in error, the actual limit for both, CH and CN, being at F8. We have further investigated the equilibrium conditions for the molecules of CH and CN with their constituent atoms, and have attempted to explain why the two bands disappear in the same spectral class, notwithstanding the difference between their heats of dissociation.

2. The heat of dissociation of the CH molecule has not been determined spectroscopically, since no formula for the band-heads is available. We shall therefore use values determined chemically. According to Fajans,¹¹ the work required for separating the components of a CH molecule is in the neighborhood of 90 k cal/mol. More recent determinations give slightly higher values: Mecke¹² found for the C—H bond the following energies: 107 k cal in formaldehyde, 93 k cal in acetaldehyde, 110 k cal in benzaldehyde, 115 k cal in methane. Ellis¹³ found 97 k cal/mol in hexane, and various values up to 117 k cal for other molecules. We shall adopt here as approximate energy of dissociation of CH, 110 k cal/mol.

The heat of dissociation of CN has been determined spectroscopically at 220 k cal—in good agreement with the thermo-chemical methods, which give 210 k cal. We shall use this latter value in our computations.

⁵ B. Lindblad, reference 4; R. Wildt, *Zeits. f. Physik* **54**, 856 (1929).

⁶ H. Shapley, *Harvard Observatory Bulletin* No. 805, 1924; A. V. Douglas, *Monthly Notices of the Royal Astronomical Society* **90**, 798 (1930); C. H. Payne, *Stellar Atmospheres* p. 168, 1925.

⁷ H. Shapley, *Harvard Observatory Bulletin*, No. 862, 1928; C. T. Elvey and R. Zug, *Astrophys. J.* **70**, 243 (1929).

⁸ S. Rosseland, *Astrophysik* p. 181, 1931; C. H. Payne, *Stellar Atmospheres* pp. 63, 168, 1925.

⁹ W. C. Rufus, reference 2; A. J. Cannon, *Harvard Annals* **91**, 7 (1918); R. Wildt, reference 5.

¹⁰ S. Rosseland, reference 8; R. Wildt, reference 5.

¹¹ K. Fajans, *Ber. d. Deutsch. Chem. Gesell.* **53**, 643 (1920).

¹² R. Mecke, *Nature* **125**, 526 (1930).

¹³ J. W. Ellis, *Phys. Rev.* **33**, 27 (1929).

3. The molecule CH gives rise, in stellar spectra, to two bands situated roughly at $\lambda 4300$ and $\lambda 3900\text{A}$. The first of these is superposed over a region containing many strong atomic lines, and the blend of all these lines, atomic and molecular, constitutes the "G-band" of Fraunhofer, prominently seen in the spectrum of the Sun. We have investigated this band in stars of classes F and G. It results from the transition ${}^2\Delta - {}^2\Pi$; the lower level ${}^2\Delta$ of the band at $\lambda 4300$ is probably the ground-level of the CH molecule.

The identification of the stellar band with CH was made by Newall, Baxandall and Butler.¹⁴ It extends from about $\lambda 4250$ to $\lambda 4320$ ¹⁵—a region which is especially rich in strong atomic lines [Various strong lines of Fe, Ti, Ca, Cr, Mn, Sc II etc.]. These atomic lines, superposed over the rotational lines of the CH band, produce numerous blends distributed over the whole region.

Table I gives the number of lines of various Rowland intensities (greater than 2) in the region $\lambda 4250$ to $\lambda 4320$.¹⁵ It is obvious that in the solar spectrum (class G0, dwarf) the contribution of the CH lines to Fraunhofer's "G-band" is much inferior to that of the atomic lines. Consequently, on plates taken with small dispersion, and especially with objective-prisms, the blended appearance of the region near $\lambda 4300$ is almost entirely due to atomic lines.

TABLE I

Rowland intensity	15	8	7	6	5	4	3	2	3-blends	2-blends
No. of atomic lines	1	3	1	2	3	8	18	48	—	—
No. of CH lines	—	—	—	—	—	1	3	16	3	12

The observable bands of CN lie in two different spectral regions: those corresponding to the electronic transition ${}^2\Sigma - {}^2\Sigma$ fall between $\lambda 3590$ and $\lambda 4606$; the others, corresponding to the transition ${}^2\Sigma - {}^2\Pi$, are in the red,¹⁶ near $\lambda 7000$. The lower level of the two transitions (${}^2\Sigma$) is the same for both band-systems. Little is known at present concerning the bands in the red. Those of shorter wave-length are listed in Table II. In stellar spectra these bands have been

TABLE II

n''	0	1	2	3	4	5	6	7
n'								
0	3883	4216	4606					
1	3590		4197	4578				
2				4181	4553			
3						4532		
4							4515	
5								4503

¹⁴ H. F. Newall, F. E. Baxandall and C. P. Butler, Monthly Notices of the Royal Astronomical Society **76**, 640 (1916).

¹⁵ C. E. St. John, C. E. Moore, L. M. Ware, E. F. Adams, H. D. Babcock, Revision of Rowland's Preliminary Table of Solar Wave-Lengths, 96, 1928.

¹⁶ P. W. Merrill, Scientific Papers of the Bureau of Standards, No. 318, 1918.

observed by Shane,¹⁷ Hale, Ellermann and Parkhurst,¹⁸ and by Rufus.¹⁹ The bands most convenient for study with the Bruce spectrograph (used with the 40-inch refractor of the Yerkes Observatory) are the ones near $\lambda 4216$ (0-1), and $\lambda 4197$ (1-2). There are, as in the case of CH, numerous blends with atomic lines, and the contribution of the CN lines is relatively insignificant, as Table III shows.

TABLE III. *Region $\lambda 4190$ to $\lambda 4210$.*

	8	6	5	4	3	2	1	0
Rowland intensity	8	6	5	4	3	2	1	0
No. of atomic lines	1	1	2	5	8	7	17	17
No. of CN lines (certain)	—	—	—	—	—	1	1	2
No. of CN lines (uncertain)	—	—	—	—	—	1	1	5

4. In view of the great predominance of atomic lines in both regions, it is useless to investigate the appearance of the whole band on plates of small dispersion. The obvious method is to find, within the region considered, one or more individual lines of CH which are unblended with atomic lines. The linear dispersion of our spectrograph is 30A/mm at $\lambda 4500$.

For the CH band we examined the wave-lengths $\lambda 4310.4$ to $\lambda 4312.7$. Here the rotational lines of the band appear almost pure, as we see in Table IV (in which the lines fainter than Rowland's int. 0 have been omitted). We have

TABLE IV.

CH Lines	Int.	Atomic lines	Int.
4310.38	2	4310.47	?
10.56	0	10.71	?
10.99	1	10.90	?
11.17	2	11.51	Fe CH
11.45	2	12.20	?
11.72	2	12.56	Mn
12.09	2		
12.15	1		
12.71	0		

also used the line $\lambda 4293.12$ of CH, intensity 3; but its proximity to $\lambda 4292.3$ (Fe, int. 2), $\lambda 4294.1$ (Ti II, Fe, int. 2+5) and $\lambda 4293.04$ (? , int. 2) makes it less suitable than the region at $\lambda 4311$. The line $\lambda 4303.942$ (CH, int. 4) although blended with $\lambda 4303.84$ (? , int. 2), $\lambda 4303.6$ (Nd II, int. 1), $\lambda 4304.4$ (CH, int. 1) and $\lambda 4304.57$ (CH, Fe, int. 2), is mostly due to the band, and has therefore been used in the estimates.

For the CN band we have used the line $\lambda 4192.574$ (CN, int. 2), which lies between $\lambda 4195.342$ (Fe, int. 5) and $\lambda 4191.5$ (Fe, int. 6+3). We have also examined $\lambda 4197.102$ (CN, int. 2), lying between $\lambda 4196.7$ (Fe, int. 1) and $\lambda 4198.06$ (Fe, int. 2).

In order to be certain of the faint band-lines, we have used for most of our spectrograms Eastman Process high-contrast plates. The actual esti-

¹⁷ C. D. Shane, Lick Observatory Bulletin 10, 79 (1919).

¹⁸ G. E. Hale, F. Ellermann and J. A. Parkhurst, Publications of the Yerkes Observatory 2, 251 (1903).

¹⁹ W. C. Rufus, Publications of the Observatory, University of Michigan 3, 258 (1923).

mates, recorded in Tables V and VI, were made with the aid of a comparator fitted with a Bausch and Lomb wide-angle microscope. A half-silvered optical beam-divider made it possible to compare (or measure) two spectrograms simultaneously. In all estimates the solar spectrum was used as standard. Tables V and VI show that the bands of CH and of CN disappear at about

TABLE V. CH band.

Star	Absolute magnitudes ²⁰	Description of CH band
<i>Spectral class G5</i>		
ϵ Gem	-1.4	Stronger than in the Sun
α UMa	+0.4	Stronger than in the Sun
η Dra	+0.7	Stronger than in the Sun
μ Her	+3.7	Stronger than in the Sun
<i>Spectral class G0</i>		
α Aqr	-2.8	Fainter than in the Sun
ϵ Leo	-0.9	About the same intensity as in Sun
α Aur	+0.1	About the same intensity as in Sun
5 Ser	+3.5	A little less strong than in Sun
13 Cet	+3.8	Same as in Sun
η Cor	+4.3	Same as in Sun
<i>Spectral class F8</i>		
γ Cyg	-3.0	Very uncertain. Hardly visible ²¹
α UMi	-3.0	Extremely faint
δ CMa	-2.9	Extremely faint
ϵ Hya	+2.1	Faint
26 Dra	+4.0	Faint
99 Her	+4.4	Faint
<i>Spectral class F5</i>		
ρ Pup	-2.1	No trace
ϵ Aur	-2.0	No trace
α Per	-1.3	No trace
41 Cyg	-1.1	No trace
α CMi	+3.2	Perhaps very faint
10 UMa	+3.2	No trace
θ Cyg	+3.4	No trace
γ Ser	+4.3	No trace
<i>Spectral Class F2</i>		
π Sgr	-0.8	No trace
<i>Spectral class F0</i>		
20 CVn	-1.4	No trace
γ Cap	-0.7	No trace
20 Per	+2.5	No trace

the same place in the spectral sequence, in class F8. There seems to be a definite indication that the CH band is stronger in dwarfs than in giants (cf. Sun and α Aquarii). This agrees well with theory. It is surprising, however, that the intensity of both bands, especially that of CH, decreases so rapidly as we pass from G0 (temperature²² about 6200°K) to F5 (temperature 7200°K). This effect is very strikingly shown in Fig. 1: in the solar spectrum the band is very strong, while in Procyon (α Canis Minoris), a dwarf of class F5, it can hardly be seen.

²⁰ W. S. Adams, A. H. Joy, G. Strömberg and C. G. Burwell, *Astrophys. J.* **53**, 13 (1921).

²¹ This agrees with: Lockyer and Baxandall, *Philosophical Transactions of the Royal Society*, (A), **201**, 205 (1903), whose list of lines in α Cygni does not contain 4303.9 (CH, int. 4) and 4293.1 (CH, int. 3).

²² We have adopted here the temperature scale of Brill, in agreement with Wildt (reference 5), although a slightly lower scale would probably have been preferable.

5. It is clear from the foregoing that it is not possible to consider all of Fraunhofer's G-band as being caused by CH. Even in the solar spectrum the total intensity of the molecular lines is relatively small. In the past the distinction between molecular and atomic lines has not always been made. In-

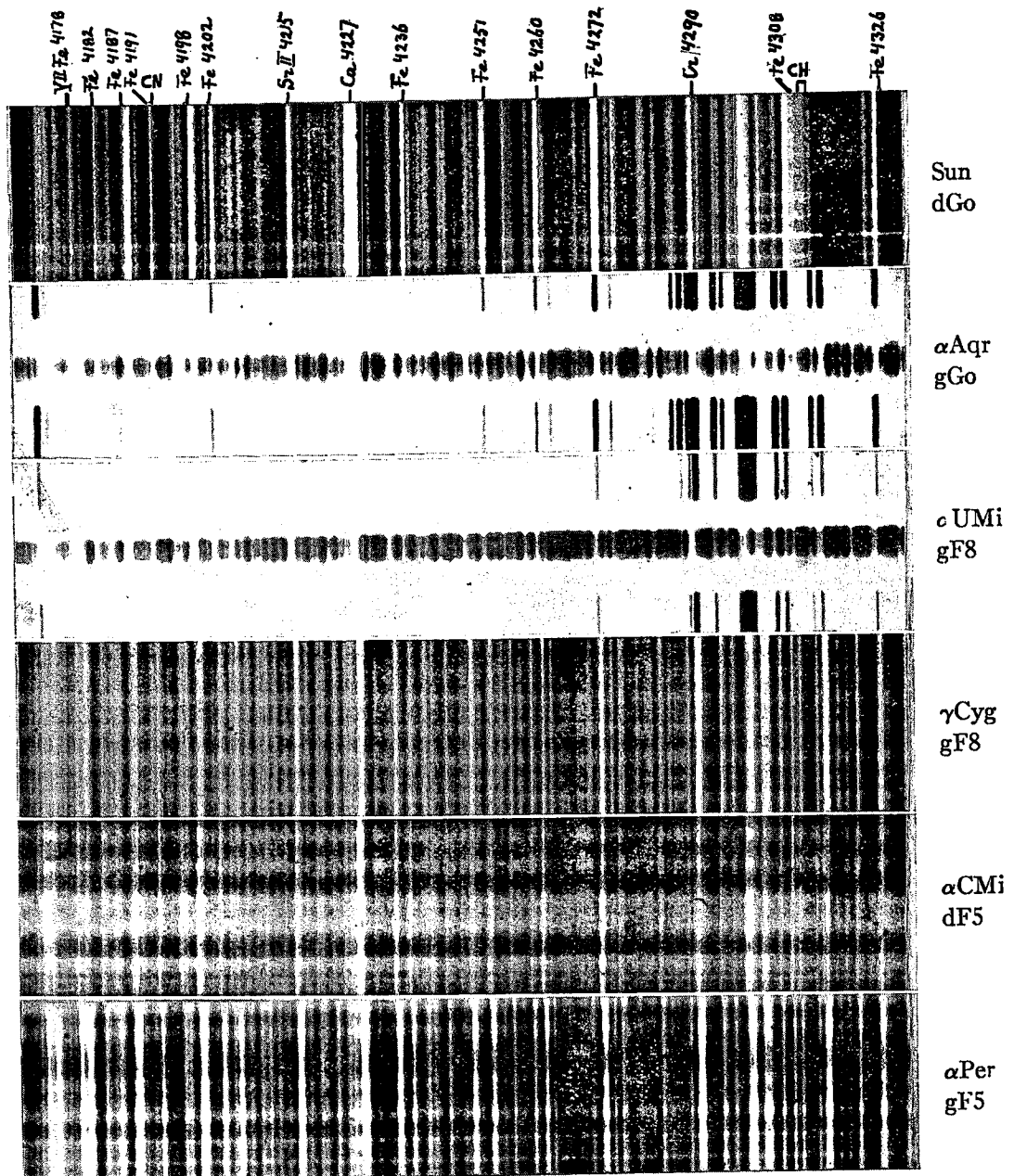


Fig. 1. Spectra of Sun and five stars, showing the region $\lambda 4170$ to $\lambda 4330$. The lines of CH and CN which were used in this investigation are marked on the upper margin. Two of the stellar spectra show the comparison lines of Ti and of Fe.

vestigations made prior to the work of Newall, Baxandall and Butler refer to the whole region of the G-band, and do not necessarily apply to the CH molecule. Thus, in the Henry Draper Catalogue²³ we read: "Class F0. Typical stars δ Geminorum and α Carinae. . . . The lines 4305.8, 4308.0 and 4309.9

²³ Harvard Annals 91, 7 (1918).

TABLE VI. CN band.

Star	Absolute magnitudes	Description of CH band
α Aqr	-2.8	About the same as in Sun
ϵ Leo	-0.9	About the same as in Sun
α Aur	+0.1	?
	<i>Spectral class F8</i>	
γ Cyg	-3.0	Extremely faint
α UMi	-3.0	Extremely faint
δ CMa	-2.9	Extremely faint
	<i>Spectral class F5</i>	
ϵ Aur	-2.0	No trace
α Per	-1.3	No trace
α CMi	+3.2	Perhaps very faint
	<i>Spectral class F2</i>	
π Sgr	-0.8	No trace

and other lines, which form the absorption band called G by Fraunhofer, are faint and inconspicuous". It is certain²⁴ that the line $\lambda 4305.8$ is Sc II 4305.715 (int. 2) and Ti 4305.92 (int. 4), rather than CH 4305.85 (int. 1); line $\lambda 4308.0$ is identical with Ca 4307.75 (int. 3) and Fe 4307.91 (int. 6), rather than with CH 4308.05 (int. 0) and CH 4308.18 (int. 1); line 4309.6 is Fe 4309.38 (int. 3), $\lambda 4309.46$ (? int. 1), Y 4309.63 (int. 1) and Ce II 4309.72 (int. 1), rather than the faint CH lines $\lambda 4309.38$ and 4309.63. The band described in the Draper Catalogue is, accordingly, of atomic origin. The same is true of the Harvard descriptions for classes F2 (π Sagittarii),²⁵ F5 (α Canis Minoris,²⁶ ρ Puppis,²⁷ α Persei)²⁸ and F8 (γ Cygni and δ Canis Majoris).²⁹

It may be noted in this connection that Dunham³⁰ found no lines definitely belonging to CH in the spectrum of α Persei, photographed with high dispersion at Mount Wilson.

In a recent paper Miss A. V. Douglas³¹ has discussed the band near $\lambda 4200$ in several Cepheid variables, and has attributed it to CN. Following is a list of lines taken from the "Revised Rowland",³² within the range $\lambda 4198$ to $\lambda 4202$. The total intensity of the CN lines is seen to be negligible in comparison with that of the atomic lines (see also Table III). The latter are so closely packed that they are doubtless blended throughout the whole range. In particular, it is almost certain that the point at which Miss Douglas measured the microphotometer deflection corresponds to several atomic lines of Rowland intensity 1 and greater, while the strongest line of CN in the same interval is but 0.

²⁴ The intensities given in parentheses are from the Mount Wilson Revision of Rowland's Solar Wave-Length Tables.

²⁵ Harvard Annals 91, introduction, 7 (1918); Harvard Annals 28, 157 (1897).

²⁶ Harvard Annals 28, 157 (1897).

²⁷ Harvard Annals 91, introduction, 8 (1918).

²⁸ Harvard Annals 28, 187, remark 178 (1897).

²⁹ Harvard Annals 28, 188 (1897).

³⁰ Contributions from the Princeton University Observatory, No. 9, 1929.

³¹ Monthly Notices of the Royal Astronomical Society 90, 804 (1930).

³² The average spectral class of the stars investigated by Miss Douglas is G0 for η Aquilae, F8 for α Ursae Minoris (Polaris), and F8 for RT Aurigae. All these are giants, and we should expect their band-lines of CN and of CH to be even fainter than those of the Sun, which is a dwarf of class G0.

TABLE VII.

Atomic lines		Int.	Lines of CN	Int.
4198.06	Fe	2		
.25	Fe	4	4199.67	-1
.34	Fe	4	4199.74	-2
.64	Fe	3	4200.70	0
99.11	Fe	5	4201.07	-1
.89	Ru	1		
.99	Fe	2		
4200.46	Ni	1		
.79	Ti	1		
.93	Fe	3		
1.71	Ni Fe	1		
2.04	Fe	8		

It is probable that her results for CH are also vitiated by the same effect of blending.

This effect of blending has doubtless influenced another investigation, one by P. ten Bruggencate,³³ on the spectra of δ Cephei variables. The linear dispersion of his objective-prism was about 100A/mm at H γ . It seems, therefore, certain that the major portion of the microphotometer deflections attributed by him to CH, have in reality been caused by closely packed atomic lines.

6. We have seen in section 1, that the heat of dissociation of the CH molecule is appreciably lower than that of the CN molecule. It is therefore surprising, at first sight, that both bands disappear at the same temperature within the spectral sequence (F8, temperature about 6500°K). We shall show that this may be explained by the enormous abundance of H in the atmospheres of the stars, which causes a slowing down of the process of decomposition of CH.

In considering the equilibrium conditions of CH and CN, we shall follow the method of Wildt,³⁴ replacing in his formulae the heat of dissociation of CH by the more modern value, 110 kcal/mol, and using the same temperature of 6500°K for both molecules.

Consider a molecule AB ; let p_A , p_B and p_{AB} be the partial pressures of the constituents of the gas: A , B and AB ; and let K_p be the equilibrium coefficient at constant pressure, $p_A p_B / p_{AB}$. Then, following the formulae of Wildt, we have for

$$\text{CN} \rightarrow \log K_p = -\frac{210000}{4.541T} + 1.5 \log T + \log (1 - e^{-2940/T}) + 0.07$$

and for

$$\text{CH} \rightarrow \log K_p = \frac{110000}{4.541T} + 1.5 \log T + \log (1 - e^{-4000/T}) - 0.40.$$

Computation gives for $T = 6500^\circ$

$$\log K_p^{\text{CN}} = -1.7 \quad \log K_p^{\text{CH}} = 1.3.$$

³³ Annalen v. d. Bosscha-Sterrenwacht, Lembang (Java) 5, 1 (1931).

³⁴ R. Wildt, reference 5.

From the definition of the coefficient K_p , it follows that

$$\log \frac{p_{\text{CH}}}{p_{\text{CN}}} = \log \frac{K_p^{\text{CN}}}{K_p^{\text{CH}}} + \log \frac{p_{\text{H}}}{p_{\text{N}}}.$$

The ratio $p_{\text{H}}/p_{\text{N}}$ is not accurately known; but H. N. Russell³⁵ has found that in the reversing layer of the Sun hydrogen is about 10^4 times more abundant (by number of atoms) than nitrogen. The total mass of the hydrogen atoms, per unit area, exceeds that of the nitrogen atoms by a factor of about 10^3 . Since the partial pressure depends upon the concentration, it is probably not exaggerated to assume

$$\log \frac{p_{\text{H}}}{p_{\text{N}}} = 3.$$

This gives

$$p_{\text{CH}} = p_{\text{CN}} \quad (\text{at } T = 6500^\circ \text{K}).$$

The simultaneous disappearance of CN and CH may thus be explained.

It should be remembered in this connection that the coefficient of absorption of CH is probably greater than that of CN. The violet cyanogen bands result from an electronic transition of the type ${}^2\Sigma - {}^2\Sigma$, while the hydrocarbon band corresponds to ${}^2\Delta - {}^2\Pi$. The probability of the latter transition is greater than that of the former, which may be the reason why, in spectral classes G0 and F8, the band of CH is stronger than that of CN.

Professor H. N. Russell has called our attention to the fact that the CN band at 3883 (not investigated by us) is far stronger than that at 4216, and may perhaps persist higher up in the spectral sequence. However, T. Dunham Jr. found no trace of the 3883 band in the star Persei α (Contribution from the Princeton University Observatory 9, 6 (1929)).

³⁵ H. N. Russell, *Astrophys. J.* 70, 56 (1929). The author states that the values for H and N are uncertain, and they merely indicate the order of magnitude concerned.

