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MOLECULAR LINES FROM THE LOWEST STATES OF DIATOMIC
MOLECULES COMPOSED OF ATOMS PROBABLY PRESENT
IN INTERSTELLAR SPACE

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ABSTRACT.—Attention is directed to the recent spectrographic observations of W. S. Adams by which he detected in the spectrum of the early class B star, ζ *Ophiuchi*, several sharp lines from the lowest states of the CH and CN molecules. The detection of these lines of apparent interstellar origin, the presence of which was predicted by the writer on the basis of proposed molecular identifications, has provided definite evidence of the correctness of these identifications and of the presence of CH and CN in interstellar space. Comment is then made upon the possibility that other unidentified interstellar lines may be due to absorption by diatomic molecules.

In the second section of the publication a brief summary is given of the observational work and the discussions in connection with the presence of molecules in interstellar space, culminating in the results of Adams mentioned above.

The third section presents the results of a systematic examination of laboratory data for the purpose of obtaining the wave-lengths of the possible molecular interstellar lines, namely the lines arising from the lowest states, of over twenty-five of the more common diatomic molecules. These wave-lengths, obtained from some fifty articles on the analysis of band spectra, are given in tabular form.

The fourth and final section opens with a list of all the interstellar lines known at present. It is emphasized that spectrograms taken with the relatively powerful three-prism spectrograph at Victoria have barely revealed the sharp CH and CN lines under the most favourable conditions, and it is concluded that, to photograph these lines satisfactorily, a spectrograph with dispersion and resolving power comparable to the coude instrument at the Mount Wilson Observatory is necessary.

The results of Adams, showing that only the lowest and next higher rotational states of CN are sufficiently populated to give interstellar lines, are of particular interest. They allow the determination of a "rotational" temperature for the region where the CN absorption takes place. This temperature, 273K, is compared with the temperatures estimated by Eddington for matter in interstellar space.

Evidence is put forward which indicates that, if the four as yet unidentified sharp interstellar lines* are due to absorption by diatomic molecules, these are probably hydrides. In the possible cases that the three strongest of these lines, or all four of them, are due to the same diatomic molecule, the vibrational constants of the upper electronic state concerned in the absorption by this hypothetical molecule are calculated. These constants are found to correspond reasonably closely to those of diatomic hydrides. Reasons are given for believing that, if Merrill's relatively diffuse interstellar lines in the yellow and red are due to diatomic molecules, these are probably molecules with neither very low nor very high moments of inertia, but those with intermediate values, for which the rotational constant B is around 0.5 to 1.0 cm.⁻¹

SECTION I—INTRODUCTION

Recent observational results of W. S. Adams at the Mount Wilson Observatory¹ have furnished conclusive evidence that certain sharp lines of interstellar character, occurring in the spectra of several early-type stars, are due to absorption by the diatomic molecules CH and CN. These observations have stimulated interest in the important problems connected with the constitution and physical state of the material existing in interstellar space. A number of the interstellar lines found during the last few years at the Mount Wilson Observatory were promptly identified by their discoverers with the

¹ *Harvard Announcement Card*, No. 526, 1940

Ap. J., **93**, 11, 1941; *Mt. W. Cont.*, No. 638.

* See footnote added in proof on p. 269.

absorption lines expected from atoms known to be reasonably abundant cosmically (Ca I, K I and Ti II), and, as mentioned above, certain others have recently been shown to be due to molecular absorption. Nevertheless, since 1934 the discovery of new absorption features has more than kept pace with their identification, so there remain at the present time eleven* such features, some sharp and some diffuse, which have not yet been identified. The positive identification of even one of these would add significant observational data on the constitution of interstellar material.

Laboratory data on the possible interstellar absorption lines arising from nearly all the known elements in atomic form (both neutral atoms and those in several successive stages of ionization) are almost complete. Hence it is improbable that any of the above mentioned eleven lines are due to atoms or atomic ions in gaseous form. In view of the evidence in favour of the existence of CH and CN in interstellar space, it is not at all unlikely that at least some of these lines are due to molecular compounds, and most probably to diatomic molecules. However, even if this is so, it is not necessarily possible to identify them at the present time, because laboratory results on the spectra of diatomic molecules are much less complete than those on atomic spectra. There are so many more diatomic molecular combinations possible than there are atoms that not all possible diatomic molecules have yet been studied in the laboratory. Also, not all possible band systems due to known molecules have been produced in the laboratory, and many band systems due to common molecules have been photographed only with spectrographs of moderate dispersion. Such low dispersion spectrograms have made it possible to obtain only an analysis of the vibrational structure of these systems, not the more involved rotational structure. A virtually complete analysis of the rotational structure of a band system is required before the wave-lengths of the one or more lines likely to appear in interstellar absorption can be accurately determined. Recently a search for possible molecular identifications of previously unidentified interstellar lines was carried out by the writer², in the course of which close coincidences in wave-length were found between sharp interstellar lines and certain molecular lines. Of the additional number of CH, CN, and NaH lines, whose presence was predicted on the basis of identifications given in this paper, several due to CH and CN have been, as already mentioned, detected by Adams¹ in the spectrum of ζ *Ophiuchi*. In the course of the writer's systematic examination of possible identifications, data were compiled on bands arising from the ground states of some twenty-five or more diatomic molecules composed of atoms which are, cosmically, relatively abundant. Except in the cases of the three molecules CH, CN, and NaH, no coincidences in wave-length between molecular and interstellar lines, close enough to be considered of real significance, have appeared. The wave-length material collected, however, may be of value as a basis for future investigations of the existence of molecules in interstellar space, particularly since more powerful spectrographic equipment may reveal the presence of lines which have so far escaped detection. The main purpose of the present publication is the presentation and discussion of this material on the wave-lengths of lines occurring in the observable spectral region, arising from the lowest states of the common diatomic molecules.

² *P.A.S.P.*, **52**, 307, 1940.

* See footnote added in proof on p. 269.

SECTION II—HISTORICAL OUTLINE

In view of the considerable significance of the recent evidence that diatomic molecules are responsible for the production of some lines of interstellar character, it is of interest to present a brief summary of the observations and discussions leading up to the present position of the subject.

Until the year 1934, the only known interstellar lines (sometimes referred to as "detached" or "stationary" lines) occurring in stellar spectra were the *H* and *K* lines of Ca II ($\lambda\lambda 3968.47, 3933.67$), noted first by Hartmann in 1904, and the first two doublets of the principal series of Na I ($\lambda\lambda 5895.92, 5889.95; 3302.99, 3302.32$), investigated in 1919 and 1921 by Miss Heger. Subsequent discoveries of interstellar lines have been due wholly to the Mount Wilson observers. First Merrill³, in 1934, found in the red and yellow regions of the spectra of numerous early-type stars four fairly diffuse lines of apparent interstellar origin ($\lambda\lambda 5780.55, 5797.13, 6283.91, 6613.9$). A later study, by Merrill and O. C. Wilson⁴, added two fainter diffuse lines in the red ($\lambda\lambda 6202.99, 6269.99$); and previously a still more diffuse feature in the violet ($\lambda 4430$) had been noted. The latter was extensively studied and its interstellar origin was confirmed by Beals and Blanchet⁵, and by Miss Sherman⁶. As yet not one of these seven diffuse interstellar lines has been identified. In 1936 Dunham and Adams⁷, examining the ultra-violet region in the spectra of some early-type stars, detected several lines ($\lambda\lambda 3072.97, 3229.18, 3241.97, 3383.76$) arising from the lowest $^4F_{3/2}$ level of the multiple ground state of Ti II. It is noteworthy that no lines originating from the 5/2, 7/2, 9/2 sub-levels of the 4F state were found. This indicates that, in a strict sense, essentially all the singly ionized titanium atoms responsible for the absorption are in their lowest possible energy state, and that therefore transitions between these four sub-levels, which are normally forbidden, must be taking place in interstellar space. About this same time, Dunham⁸ detected interstellar lines due to atoms of K I ($\lambda\lambda 7698.98, 7664.91$) and Ca I ($\lambda 4226.73$). Also, he and Adams⁸ noted four other sharp lines, apparently interstellar in origin, ($\lambda\lambda 4300.32, 4232.58, 3957.74, 3934.3$), for which no chemical identification was apparent. More recently, Adams⁹ recorded the discovery of still another similar sharp absorption line in the spectrum of ζ *Ophiuchi* at $\lambda 3874.6$. An interesting and fruitful method of investigating interstellar gases has been applied within the last few years by Struve and his co-workers at the McDonald Observatory^{10a}. Using a nebular spectrograph, they have succeeded in photographing in certain restricted Milky Way regions *emission* lines of H (H α , $\lambda 6562$), O II ($\lambda 3727$), N II ($\lambda\lambda 6548, 6584$) and occasionally O III ($\lambda\lambda 5007, 4959$). These lines are presumably due to emission by atoms in interstellar space. This brief outline of the main observational results in connection with the discovery of interstellar lines includes reference to those obtained up to the very recent results of Adams¹ and of Dunham. As well as detecting in the spectrum of ζ *Ophiuchi* three lines due to CH in the $\lambda 3890$ region and the *R*(1) line of the $\lambda 3883$ CH band at $\lambda 3874.02$, to which more detailed reference is made later, Adams discovered two new sharp apparently interstellar lines at $\lambda\lambda 3745.33$

³ P.A.S.P., 46, 266, 1934.

⁴ Ap. J., 87, 375, 1938; Mt. W. Cont., No. 582.

⁵ M. N., 98, 398, 1938.

⁶ Ap. J., 90, 630, 1939.

⁷ P. Am. A. S., 9, 5, 1937.

Nature, 139, 240, 1937.

⁸ P.A.S.P., 49, 26, 1937.

⁹ Annual Report of the Director of Mount Wilson Observatory for 1938-39, p. 23.

^{10a} Struve, Eleventh Joseph Henry Lecture to the Philosophical Society of Washington, J. Wash. Acad. Sci., 31, 217, 1941.

and 3579.04. As yet there is no identification apparent for the latter two lines.* Dunham^{9b} measured the intensities of the interstellar $\lambda 4300.31$ CH line and $\lambda 3874.61$ CN line in the spectra of the seven early B-type stars, *o Persei*, *z Persei*, *e Persei*, *x Aurigae*, χ^2 *Orionis*, *z Ophiuchi* and 55 *Cygni*. Combining these measurements with *f*-values obtained from furnace spectra of the CH and CN bands, he found that the average concentration of CH and of CN molecules between these stars and our solar system is of the order of one per cubic meter.

Although Hartmann¹⁰, in 1904, favoured the interstellar origin of the "stationary" *H* and *K* lines, and V. M. Slipher¹¹, in 1909, produced strong evidence that they arose by absorption in interstellar space, it was not until about fifteen or twenty years ago that this view was accepted as correct by astronomers in general. Since then abundant evidence of overwhelming strength has supported this conclusion. Perhaps the first definite reference in print to the possible existence of simple molecules in interstellar space was that of Russell¹², in 1935, following the discovery by Merrill of the diffuse interstellar lines. Russell suggested that these might be due to absorption by molecules. Subsequent contributions to this subject are those of Eddington¹³, Swings^{14, 15}, Saha¹⁶, Swings and Rosenfeld¹⁷, Eyster¹⁸, and McKellar². Eddington's general conclusion, like Russell's was that molecules, no doubt, were formed and could exist in interstellar space. In his valuable papers, Swings extended to very long wave-lengths (up to $10,000\mu$) the earlier calculations of Eddington¹⁹ on the "Equivalent Temperature", T_λ , of radiation in interstellar space. He showed that, beyond wave-length 100μ , T_λ is less than $5^\circ K$; hence that probably only the few lowest rotational states of any molecules present would be populated appreciably. He also suggested that two of the diffuse features observed by Merrill ($\lambda\lambda 6283.91$, 6613.9) might be due to CO_2 , since they agreed fairly well with calculated wave-lengths of two vibration-rotation bands of this molecule. Later observations made at Mount Wilson⁴ revealing the absence of the presumably more intense lower harmonics, the "Venus" bands, of CO_2 , indicated that this suggested identification could not be true. Saha¹⁶ suggested that two of Merrill's broad lines, $\lambda\lambda 6283$ and 5780 , were due, respectively, to the Na_2 and NaK molecules. More than adequate evidence of the error of these identifications was advanced by Swings and Rosenfeld¹⁷ and by Eyster¹⁸. Swings and Rosenfeld made a further valuable contribution in adapting approximately to conditions of interstellar space the equation for dissociative equilibrium of molecules in stellar atmospheres. From this they deduced that numerous diatomic molecules made up of cosmically abundant atoms, for example CH, CN, OH, and NH, should not be much less abundant than sodium or singly ionized calcium atoms in interstellar space. Also they noted the close agreement in wave-length between the $R_2(1)$ line at $\lambda 4300.3$ in the $\lambda 4315$ $0,0 \rightarrow 2\Delta$, 2Π band of CH and the sharp unidentified interstellar line at $\lambda 4300.32$. The lowest rotational state of CH is double, the separation being 18 cm^{-1} or 0.0022 volts. The above-mentioned line has as its initial state in absorption the lower of these two sub-levels, while the $R_1(1)$ line at $\lambda 4303.9$ arises from the upper of the two. Swings and

^{9b} *P. Am. A. S.*, **10**, 123, 1941.

¹⁰ *Ap. J.*, **19**, 268, 1904.

¹¹ *B. Lowell O.*, **2**, 1, 1909.

¹² *M. N.*, **95**, 635, 1935.

¹³ *Observatory*, **60**, 99, 1937.

¹⁴ *M. N.*, **97**, 212, 1937.

¹⁵ *Annales d'Astrophysique*, **1**, 39, 1938.

¹⁶ *Nature*, **139**, 840, 1937.

¹⁷ *Ap. J.*, **86**, 483, 1937.

¹⁸ *Ap. J.*, **86**, 486, 1937.

¹⁹ *Internal Constitution of the Stars*, Cambridge University Press, 1926, Chapter XIII.

* See footnote added in proof on p. 269.

Rosenfeld indicated that the $\lambda 4303.9$ line might be expected but that its detection might be rendered difficult by blending with the O II line at $\lambda 4303.82$. Actually, this O II line does not appear strongly in most early B-type spectra, and the recent observation of the CN interstellar lines by Adams¹ makes it appear that the upper of the lowest doublet rotational level of CH, although only 0.0022 volts above the lowest, would not be appreciably populated, so the $\lambda 4303.9 R_1(1)$ line would not be expected to occur. The paper by McKellar² emphasized the above-mentioned assignment of the $\lambda 4300.32$ interstellar line to CH by Swings and Rosenfeld, and pointed out additional coincidences in wave-length between the interstellar lines at $\lambda 3874.6$ and $\lambda 3934.3$ with lines expected from the CN and NaH molecules, respectively. Further, it was found possible to predict the occurrence of additional CH, CN, and NaH lines arising from the lowest states of these molecules, and it was suggested that the observation of these would provide a definite proof of the correctness of the assignment of these lines to the diatomic molecules in question. Then followed the noteworthy achievement of Adams¹, who actually found in the spectrum of ζ *Ophiuchi* several of these predicted CH and CN lines and thereby established beyond question the molecular origin of a number of the sharp lines of interstellar character.

TABLE 1. COMPARISON OF WAVE-LENGTHS OF CH AND CN LINES MEASURED IN THE LABORATORY AND IN THE SPECTRUM OF ζ *OPHIUCHI*

Molecule	Band	Line	Laboratory λ	λ in ζ <i>Ophiuchi</i> (Adams)	$\lambda_{\text{star}} - \lambda_{\text{lab.}}$
CH	$\lambda 4315$	$R_2(1)$	4300.31A	4300.34A*	+0.03A
CH	$\lambda 3870$	${}^rQ_{12}(1)$	3890.23	3890.25	+0.02
CH	$\lambda 3870$	$Q_2(1) + {}^oR_{12}(1)$	3886.39	3886.44	+0.05
CH	$\lambda 3870$	$R_2(1)$	3878.77	3878.81	+0.04
CN	$\lambda 3883$	$R(0)$	3874.61	3874.62	+0.01
CN	$\lambda 3883$	$R(1)$	3874.00	3874.02	+0.02
CN	$\lambda 3883$	$P(1)$	3875.77	3875.77	0.00†

The mean wave-length of this line in the spectra of ξ *Persei*, χ^2 *Orionis*, and 55 *Cygni* is 4300.32A.

There is shown in Table 1 a comparison of the wave-lengths of the CH and CN lines occurring in the spectrum of ζ *Ophiuchi*, as measured by Adams, with the best laboratory values of these wave-lengths. References to sources of the laboratory wave-lengths are given in Tables 2 and 3. It is seen that the agreement in wave-length is extremely good. The CH and CN lines in the spectrum of ζ *Ophiuchi* were corrected for the displacements of the interstellar *H* and *K* lines of Ca II. Thus, as Adams has suggested, the small systematic difference in wave-length shown in the last column may be explained alternatively as due to a difference in the two systems of wave-lengths or a difference of some 2 km/sec. between the radial velocities of the diatomic molecules and Ca II atoms. Further wave-length measurements, both laboratory and stellar, will doubtless settle this point.

Some data concerning the intensities of the CH band lines are of interest. It should be borne in mind that all four interstellar CH lines arise from the *same* rotational level, the lowest possible for this molecule. First, considering the three lines of the $\lambda 3870$

† See footnote on p. 271.

$^2\Sigma$, $^2\Pi$ band, $^2Q_{12}(1)$ at $\lambda 3890.23$, $Q_2(1) + ^4R_{12}(1)$ at $\lambda 3886.39$, and $R_2(1)$ at $\lambda 3878.77$, since the population of their common initial level is necessarily the same for each, their relative intensities should be exactly as their "intensity factors" (see p. 268, equation 2), which are, respectively, 10, 15, and 5^{19a} . Adams¹ has estimated their relative intensities as 2 : 3 : 1, exactly in accord with this expectation. Second, in all laboratory sources of the CH bands, such as burning hydrocarbon gases and discharge tubes containing organic vapours, the $\lambda 4315$ band appears with somewhat greater intensity^{19b} than the $\lambda 3870$ band, although insofar as the writer is aware their relative intensity has not actually been measured. Therefore we should expect that the $\lambda 4300.31$ line, representing the $\lambda 4300$ band, should have an intensity somewhat greater than that of the three lines near $\lambda 3890$ combined, which represent the $\lambda 3870$ band. Adams has indicated this actually to be the case in the spectrum of ζ *Ophiuchi* by estimating the intensity of $\lambda 4300.31$ relative to the sum of the other three as 8 to 6.

In this connection it would appear to be very worthwhile to measure the equivalent widths of the four interstellar CH lines in the spectra of a number of stars. The intensity of the $\lambda 4300.31$ line relative to the combined intensities of the three lines near $\lambda 3890$ should be constant. The average of this ratio obtained from numerous stellar spectra would yield probably the most accurate obtainable value of the relative strengths or absorption coefficients of the $^2\Delta$, $^2\Pi$ and $^2\Sigma^-$, $^2\Pi$ electronic transitions in CH. Good laboratory data of this nature are very meagre. A determination as above would avoid such difficulties attendant upon intensity measurements of laboratory emission bands as the dependence of the population of the initial levels on the mode of excitation, and the summation, for each band system, of the intensities of the many band lines produced.

SECTION III—COMPILATION OF WAVE-LENGTHS OF POSSIBLE INTERSTELLAR MOLECULAR LINES

The scope of the compilation of diatomic molecular lines given in this paper is limited by several conditions. Some of these follow from the low "effective" temperature of matter in interstellar space, others depend on judgment, the extent of laboratory work done on spectra of the various molecules, and the availability of the results of this work to the writer.

Only those molecules were considered, at least one atomic constituent of which is reasonably abundant astrophysically, and which, therefore, it is considered might possibly be present in interstellar space. It has been demonstrated that, due to conditions existing in interstellar space, only the lowest molecular energy level or (e.g. the case of CN) those very close to it will be appreciably populated. Therefore only lines originating on these levels need be considered.* It is clear then, that for a given molecule we are concerned only with those band systems whose lowest electronic state is the normal state of the molecule. Furthermore only those bands in the system arising from the zero vibrational level of this state are of interest, namely the $v',0$ bands, and a still further restriction may

^{19a} Cf. reference No. 45, p. 177.

^{19b} e.g., see reference No. 45, Plate II.

* This is doubtless so for heteronuclear molecules possessing a permanent dipole moment. However, for homonuclear molecules such as C_2 , Na_2 , K_2 , with no permanent dipole moment, pure rotational transitions are forbidden. Hence in considering that only the very lowest states of the latter type of molecule are populated, we assume these forbidden transitions occur under conditions existing in interstellar space (as Dunham found to be so in the somewhat analogous case of Ti II atoms). Whether such an assumption is justified has not been conclusively settled as yet, so it is open to question.

be imposed by including only the one, two, or three such bands that, according to the Franck-Condon principle and laboratory data (which are invariably in accord with this principle), are the most intense ones arising from the $v''=0$ level. In a band that fulfills all these conditions, only the individual line or lines arising from rotational quantum states some 5 cm^{-1} or closer to the lowest one would be expected. In the case of hydride molecules, the moment of inertia is low, the rotational states are correspondingly far apart, and so usually only the one, two, or three lines from the lowest rotational state are of interest in seeking possible interstellar lines. For heavier molecules with greater moments of inertia, there may be several rotational states within 5 cm^{-1} of the lowest and so a correspondingly greater number of band lines might occur. Only band systems in the spectral region available to astronomers for photographic study need be considered. This region has been taken as extending from $3000\text{\AA}$ to $10,000\text{\AA}$. In several cases, to be mentioned later, the only band systems involving the normal electronic state of very common diatomic molecules lie in the inaccessible ultra-violet below $3000\text{\AA}$. As previously mentioned, a fairly complete analysis of a band system is necessary before the lines fulfilling all the above conditions can be determined and such complete analyses have not yet been carried out for some band systems which might otherwise be of interest. Finally, the writer, although having access to many, has not found it possible to consult all the periodicals and publications in which papers on band spectra have been published, so the scope of the material collected has been limited somewhat, although it is hoped not seriously, by this circumstance.

As bearing upon the likelihood of the occurrence of the lines of a given diatomic molecule as interstellar lines, several factors may be examined. Of primary importance is the abundance of the molecule in interstellar space. The well-known²⁰ expression derived for the case of dissociative equilibrium between diatomic molecules and their constituent atoms in stellar atmospheres was modified by Swings and Rosenfeld¹⁷, to apply at least roughly to the conditions in interstellar space, by introducing the dilution factor δ used by Eddington²¹. In this form the expression is as follows:—

$$\frac{n_{AB}}{n_A n_B} = \frac{G_{AB}}{G_A G_B} \cdot \frac{r_0^2 h}{1 - e^{-\frac{\omega h}{kT}}} \left(\frac{8\pi}{\mu kT} \right)^{\frac{1}{2}} \cdot e^{\frac{D}{kT}} \cdot \delta \cdot \alpha^* \dots \dots \dots (1)$$

where n_{AB} = number of diatomic molecules made up of atoms A and B ,
 n_A and n_B = respectively, the number of atoms A and atoms B ,
 G_{AB} = the statistical weight of the normal state of molecule AB ,
 G_A and G_B = respectively, the statistical weights of the normal states of the atoms A and B ,

²⁰ Cf., Rosseland, *Theoretical Astrophysics*, Oxford University Press, 1936, Chapter 18.

²¹ Cf., reference 19, p. 382.

* (Note added in proof) Formula (1) written without the final factor α gives an abundance for CN and CH in interstellar space of only about one one-thousandth of that measured by Dunham¹⁶. Dr. P. Swings in a recent communication to the writer has suggested that the expression should be multiplied by the factor α to take into account the fact that in interstellar space photodissociation of the molecule must start from the lowest molecular state, whereas its formation can take place in any one of many excited states. Professor J. R. Oppenheimer has calculated the correction term as $\alpha = 4\pi^2 E I / h^2$ where E is the energy of collision of the two component atoms on association, I the moment of inertia of the molecule and h is Planck's constant. This factor is about 10^3 , thus accounting well for the discrepancy mentioned above. For more details regarding this correction term see Swings' article "Some Considerations Regarding Interstellar and Cometary Molecules," a Lick Observatory Bulletin now in press. The writer acknowledges with thanks the kindness of Dr. Swings in making available to him a copy of this interesting paper in manuscript form.

r_0 = the equilibrium internuclear distance between the atoms composing molecule AB ,

ω = fundamental vibrational frequency of the molecule,

μ = the reduced mass of the molecule, $\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$,

D = the heat of dissociation of the molecule,

δ = the dilution factor ($\sim 10^{15}$),

and the other symbols have their usual significance. This equation indicates at once that the number of molecules of a given kind to be expected depends not only, as one would immediately surmise, upon the abundance of its constituent atoms, but also how it depends upon the molecular constants r_0 , ω , D and μ . Thus, for example, other factors being about the same, a stable molecule with a high heat of dissociation would be relatively more abundant than a less stable one with a low value of D .

As well as the abundance of a molecule, there should be taken into account the f -values or mean oscillator strengths of the electronic transitions from the ground state²². It is clear that, for a fixed number of absorbing molecules, the strength of a given band system depends on the number of alternative transitions that can take place and on the related f -value of the transition involved in its production. Although theoretical and laboratory studies have yielded data on the number of band systems (electronic transitions) that are possible for a given molecule, and for such a molecule the relative intensities of the systems, under special excitation conditions, can be roughly estimated from laboratory results, very few experimental or theoretical determinations of f -values have been carried out even for band systems of the most common molecules. It is hoped that the meagre supply of such data at present available will be substantially augmented in the near future. Considering the rotational structure of band systems, it is perhaps unnecessary to mention that, for a given population of the lowest quantum state, relatively simple electronic transitions such as $^1\Sigma$, $^1\Sigma$ or $^2\Sigma$, $^2\Sigma$, where only one line arises from the $K'' = 0$ level, should give stronger lines than more involved transitions where several lines can arise from lowest level.

The wave-length material on band lines from the lowest molecular states is presented in two tables, the first one containing data for hydride molecules and the second for molecules other than hydrides. A third table lists those common molecules whose known band systems involving the normal electronic state lie beyond the observable spectral region.

The spectra of hydrides were listed separately because, due to the excessive cosmical abundance of hydrogen, they might be expected to be relatively plentiful compared to non-hydrides. Table 2, containing data on the spectra of seventeen hydrides, lists in successive columns: the name of the molecule; the electronic transition giving rise to the band system; the band, or vibrational transition; the individual line, or rotational transition; the laboratory wave-length of the line; and, in the last column, reference to the source of the laboratory data. In view of the great abundance of hydrogen, several hydride molecules for which wave-length data were readily procurable were included in this table, even when the atom in combination with hydrogen was known not to be among the most abundant.

²² Cf. Mulliken, *J. Chem. Phys.*, 7, 14, 1939.

The detection by Adams of the CH lines renders very promising the search, with a spectrograph of sufficient resolving power, for lines of numerous hydrides, particularly NH, OH, and SiH. The wave-lengths listed in the fourth column of Table 2 are those of lines arising from the lowest state only, for, as already mentioned, Adams' results on CH indicate that a level only 18 cm^{-1} or 0.0022 volts above the lowest is not populated sufficiently to produce an absorption line. It should perhaps be noted that, in Tables 2 and 3, where a molecule listed contains an atom or atoms having two or more isotopes, the wave-lengths given are those for the molecule involving the most abundant isotopes. An excellent and homogeneous body of data on the molecular constants of the ground states of all known diatomic molecules, including the constants ω , D , and r_0 which enter equation (1), may be found in the comprehensive Table 36 of Herzberg's recent book on molecular spectra²³, so these constants are not given in Tables 2 and 3 of the present publication.

TABLE 2. BAND LINES ARISING FROM THE LOWEST STATES OF HYDRIDE MOLECULES

Molecule	Electronic transition	Band	Line	Wave-length	Reference
LiH	$^1\Sigma, ^1\Sigma$	10,0	$R(0)$	3386.02	24
	$^1\Sigma, ^1\Sigma$	11,0	$R(0)$	3341.76	
	$^1\Sigma, ^1\Sigma$	13,0	$R(0)$	3257.38	
BH	$^1\Pi, ^1\Sigma$	0,0	$R(0)$	4328.21	25
BH ⁺	$^2\Pi, ^2\Sigma^+$	0,0	$Q_1(0)$	3791.38	26
	$^2\Pi, ^2\Sigma^+$	0,0	$R_1(0)$	3788.26	
CH	$^2\Delta, ^2\Pi$	0,0	$R_2(1)$	4300.31	27
	$^2\Sigma^-, ^2\Pi$	0,0	$^PQ_{12}(1)$	3890.23	
	$^2\Sigma^-, ^2\Pi$	0,0	$Q_2(1) + ^Q R_{12}(1)$	3886.39	
	$^2\Sigma^-, ^2\Pi$	0,0	$R_2(1)$	3878.77	
	$^2\Sigma^-, ^2\Pi$	1,0	$^PQ_{12}(1)$	3637.62	
	$^2\Sigma^-, ^2\Pi$	1,0	$Q_2(1) + ^Q R_{12}(1)$	3634.63	
	$^2\Sigma^-, ^2\Pi$	1,0	$R_2(1)$	3628.78	
	$^2\Sigma^+, ^2\Pi$	0,0	$^PQ_{12}(1)$	3146.01	
	$^2\Sigma^+, ^2\Pi$	0,0	$Q_2(1) + ^Q R_{12}(1)$	3143.15	
	$^2\Sigma^+, ^2\Pi$	0,0	$R_2(1)$	3137.53	
NH	$^3\Pi, ^3\Sigma$	0,0	$R_1(0)$	3357.83	28
OH	$^2\Sigma^+, ^2\Pi$	0,0	$P_1(1)$	3081.5	29
	$^2\Sigma^+, ^2\Pi$	0,0	$Q_1(1)$	3078.4	
	$^2\Sigma^+, ^2\Pi$	0,0	$R_1(1)$	3072.4	
	$^2\Sigma^+, ^2\Pi$	0,0	$^sR_{21}(1)$	3062.5	
OH ⁺	$^3\Pi, ^3\Sigma$	0,0	$R_3(0)$	~ 3566.5	30
NaH	$^1\Sigma, ^1\Sigma$	7,0	$R(0)$	4049.0	
	$^1\Sigma, ^1\Sigma$	8,0	$R(0)$	3990.88	31, 32
	$^1\Sigma, ^1\Sigma$	9,0	$R(0)$	3934.29	
	$^1\Sigma, ^1\Sigma$	10,0	$R(0)$	3879.29	
	$^1\Sigma, ^1\Sigma$	11,0	$R(0)$	3825.95	
	$^1\Sigma, ^1\Sigma$	12,0	$R(0)$	3774.3	
MgH	$^2\Pi, ^2\Sigma$	0,0	$R_1(0)$	5183.40	33
	$^2\Pi, ^2\Sigma$	0,0	$Q_1(0)$	~ 5187.0	

²³ *Molecular Spectra and Molecular Structure*, Prentice-Hall Inc., New York, 1939.

²⁴ Crawford and Jorgensen, *Phys. Rev.*, **47**, 932, 1935.

²⁵ Thunberg, *Z. f. Physik*, **100**, 471, 1936.

²⁶ Almy and Horsfall, *Phys. Rev.*, **51**, 491, 1937.

²⁷ McKellar, *P.A.S.P.*, **52**, 312, 1940.

^{27a} Fagerholm, *Archiv for Matematik, Astronomi och Fysik*, **27**, No. 19, 1941.

²⁸ Funke, *Z. f. Physik*, **96**, 787, 1935.

²⁹ Heurlinger, *Dissertation*, Lund, 1918.

³⁰ Loomis and Brandt, *Phys. Rev.*, **49**, 55, 1936.

³¹ Hori, *Z. f. Physik*, **62**, 352, 1930, and **71**, 478, 1931.

³² Olsson, *Z. f. Physik*, **93**, 206, 1934.

³³ Guntzsch, *Z. f. Physik*, **104**, 584, 1937, and **107**, 420, 1937.

TABLE 2. BAND LINES ARISING FROM THE LOWEST STATES OF HYDRIDE MOLECULES
—Concluded

Molecule	Electronic transition	Band	Line	Wave-length	Reference
AlH	$^1\Pi, ^1\Sigma$	0,0	$R(0)$	4257.19	34, 35, 36
	$^1\Pi, ^1\Sigma$	1,0	$R(0)$	4069.82	
AlH ⁺	$^2\Pi, ^2\Sigma$	0,0	$R_1(0)$	3610.22	37
	$^2\Pi, ^2\Sigma$	0,0	$Q_1(0)$	3612.67	
SiH	$^2\Delta, ^2\Pi$	0,0	$R_2(1)$	4123.02	38, 39, 40
KH	$^1\Sigma, ^1\Sigma$	9,0	$R(0)$	4608.22	41
	$^1\Sigma, ^1\Sigma$	10,0	$R(0)$	4546.69	
	$^1\Sigma, ^1\Sigma$	11,0	$R(0)$	4487.1	
	$^1\Sigma, ^1\Sigma$	12,0	$R(0)$	4429.26	
CaH	$c, ^2\Sigma, x, ^2\Sigma$	0,0	$R(0)$	3525.10	42
	$d, ^2\Sigma, x, ^2\Sigma$	1,0	$R_1(0)$	~4234.5	
	$d, ^2\Sigma, x, ^2\Sigma$	1,0	$^RQ(0)$	~4233.2	43
	$d, ^2\Sigma, x, ^2\Sigma$	2,0	$R_1(0)$	~4059	
	$d, ^2\Sigma, x, ^2\Sigma$	2,0	$^RQ(0)$	~4059	44, 45
	$b, ^2\Sigma, x, ^2\Sigma$	0,0	$R_1(0)$	6342.66	
	$b, ^2\Sigma, x, ^2\Sigma$	0,0	$^RQ(0)$	6342.15	
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$Q_1(0)$	6945.76	
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$R_1(0)$	6939.20	46
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$^SR_{21}(0)$	6904.50	
NiH	$^2\Delta, ^2\Delta$	0,0?	$R(2)$	6245.88	47
	$^2\Delta, ^2\Delta$	0,0?	$Q(2)$	6260.09	
	$^2\Delta, ^2\Delta$	1,0?	$R(2)$	5712.54	
	$^2\Delta, ^2\Delta$	1,0?	$Q(2)$	5724.84	
SrH	$c, ^2\Sigma, x, ^2\Sigma$	0,0	$R(0)$	3800.20	48
	$c, ^2\Sigma, x, ^2\Sigma$	1,0	$R(0)$	3619.60	
	$d, ^2\Sigma, x, ^2\Sigma$	2,0	$R(0)$	4406.05	49
	$d, ^2\Sigma, x, ^2\Sigma$	3,0	$R(0)$	4233.48	
	$d, ^2\Sigma, x, ^2\Sigma$	4,0	$R(0)$	4079.68	
	$b, ^2\Sigma, x, ^2\Sigma$	0,0	$R_1(0)$	6962.93	
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$R_1(0)$	7482.48	
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$Q_1(0)$	7473.00	
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$^SR_{21}(0)$	7315.15	50, 51
	$^2\Sigma, ^2\Sigma$	0,0	$R_1(0)$	4215.10	
BaH	$^2\Sigma, ^2\Sigma$	1,0	$R_1(0)$	4001.23	52
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$R_1(0)$	6827.40	
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$Q_1(0)$	6831.90	53
	$A, ^2\Pi, x, ^2\Sigma$	0,0	$^SR_{21}(0)$	6621.27	
	$^2\Sigma, x, ^2\Sigma$	0,0	$R_1(0)$	9041.59	54
	$^2\Sigma, x, ^2\Sigma$	1,0	$R_1(0)$	~8252	

³⁴ Eriksson and Hulthen, *Z. f. Physik*, **34**, 775, 1925.³⁵ Bengtsson and Rydberg, *Z. f. Physik*, **59**, 540, 1930.³⁶ Holst and Hulthen, *Z. f. Physik*, **90**, 712, 1934.³⁷ Almy and Watson, *Phys. Rev.*, **45**, 871, 1934.³⁸ Jackson, *Proc. Roy. Soc.*, **126**, 373, 1930.³⁹ Mulliken, *Phys. Rev.*, **37**, 733, 1931.⁴⁰ Rochester, *Z. f. Physik*, **101**, 769, 1936.⁴¹ Almy and Hause, *Phys. Rev.*, **42**, 242, 1932.⁴² Mulliken, *Phys. Rev.*, **25**, 509, 1925.⁴³ Grundstrom, *Z. f. Physik*, **75**, 302, 1932.⁴⁴ Hulthen, *Phys. Rev.*, **29**, 97, 1927.⁴⁵ Jevons, *Report on Band Spectra of Diatomic Molecules*, Physical Society, London, 1932, pp. 157-8.⁴⁶ Mulliken and Christy, *Phys. Rev.*, **38**, 611, 1930.

Also cf., reference 45, pp. 165 and 169.

⁴⁷ Gaydon and Pearse, *Proc. Roy. Soc.*, **148**, 312, 1935.⁴⁸ More and Cornell, *Phys. Rev.*, **53**, 806, 1938.⁴⁹ Watson and Fredrickson, *Phys. Rev.*, **39**, 765, 1932.⁵⁰ Grundstrom, *Z. f. Physik*, **99**, 595, 1936.⁵¹ Funke and Grundstrom, *Z. f. Physik*, **100**, 293, 1936.⁵² Fredrickson and Watson, *Phys. Rev.*, **39**, 753, 1932.⁵³ Koontz and Watson, *Phys. Rev.*, **48**, 937, 1935.

Table 3 contains data on the non-hydride molecules arranged in the same general manner as in Table 2. Adams' observational results, particularly his detection of the $R(1)$ line of the $\lambda 3883$ CN band, show that in interstellar space a molecular rotational state 3.78 cm^{-1} (0.00047 volts) above the lowest state is populated sufficiently to act as

TABLE 3. BAND LINES ARISING FROM THE LOWEST STATES OF MOLECULES OTHER THAN HYDRIDES

Molecule	Electronic transition	Band	Line	Wave-length	Excitation potential in cm^{-1}	Reference
C_2	$^3\Pi, ^3\Pi$	0,0	$R_3(0)$	~ 5159.12	*	54, 55
	$^3\Pi, ^3\Pi$	0,0	$R_3(1)$	5158.03		
	$^3\Pi, ^3\Pi$	0,0	$R_2(1)$	5157.14		
	$^3\Pi, ^3\Pi$	0,0	$P_3(1)$	~ 5160.4		
	$^3\Pi, ^3\Pi$	0,0	$R_1(2)$	5154.15		
	$^3\Pi, ^3\Pi$	1,0	$R_3(0)$	~ 4731.02		
	$^3\Pi, ^3\Pi$	1,0	$R_3(1)$	4730.09		
	$^3\Pi, ^3\Pi$	1,0	$R_2(1)$	4729.35		
	$^3\Pi, ^3\Pi$	1,0	$P_3(1)$	~ 4732.1		
	$^3\Pi, ^3\Pi$	1,0	$R_1(2)$	4726.90		
CN	$^2\Sigma, ^2\Sigma$	0,0	$R(0)$	3874.61	0.00	56
	$^2\Sigma, ^2\Sigma$	0,0	$R(1)$	3874.00	3.78	
	$^2\Sigma, ^2\Sigma$	0,0	$P(1)$	3875.77	3.78	
	$^2\Sigma, ^2\Sigma$	1,0	$R(0)$	3579.99	0.00	57
	$^2\Sigma, ^2\Sigma$	1,0	$R(1)$	3579.47	3.78	
	$^2\Sigma, ^2\Sigma$	1,0	$P(1)$	3580.95	3.78	
	$^3\Pi, ^2\Sigma$	2,0	Several lines	~ 6930	0.00 and 3.78	58
	$^3\Pi, ^2\Sigma$	2,0	"	~ 6951	0.00 and 3.78	
	$^3\Pi, ^2\Sigma$	3,0	"	~ 6197	0.00 and 3.78	
	$^3\Pi, ^2\Sigma$	3,0	"	~ 6216	0.00 and 3.78	
	$^3\Pi, ^2\Sigma$	4,0	"	~ 5609	0.00 and 3.78	
	$^3\Pi, ^2\Sigma$	4,0	"	~ 5625	0.00 and 3.78	
	$^3\Pi, ^2\Sigma$	5,0	"	~ 5130	0.00 and 3.78	
	$^3\Pi, ^2\Sigma$	5,0	"	~ 5144	0.00 and 3.78	
	$^3\Pi, ^2\Sigma$	0,0	$R_1(0)$	~ 4249.4	0.00	59
BO	$^3\Pi, ^2\Sigma$	0,0	$^sR_{21}(0)$	~ 4226.8	0.00	
	$^3\Pi, ^2\Sigma$	0,0	$^sQ_{21}(0)$	~ 4227.7	0.00	
	$^3\Pi, ^2\Sigma$	0,0	$Q_1(1) + ^sR_{12}(1)$	~ 4250.1	3.54	
	$^3\Pi, ^2\Sigma$	0,0	$R_1(1)$	~ 4248.9	3.54	
	$^3\Pi, ^2\Sigma$	0,0	$Q_2(1) + ^sP_{21}(1)$	4228.24	3.54	
	$^3\Pi, ^2\Sigma$	0,0	$R_2(1) + ^sQ_{21}(1)$	4227.48	3.54	
	$^3\Pi, ^2\Sigma$	0,0	$^sR_{21}(1)$	~ 4226.2	3.54	
	$^3\Pi, ^2\Sigma$	1,0	$R_1(0)$	4036.83	0.00	
	$^3\Pi, ^2\Sigma$	1,0	$^sR_{21}(0)$	~ 4016.5	0.00	
	$^3\Pi, ^2\Sigma$	1,0	$^sQ_{21}(0)$	~ 4017.2	0.00	

* In the case of the interesting C_2 molecule, it is not at present possible to state positively which of three rotational levels is the lowest one. The normal electronic state is believed to be an *inverted* $^3\Pi$ state which for intermediate and high J values is close to Hund's case b but for the lowest J values approaches case a . Since the only transitions known involving the normal state are those with other multiple ($^3\Pi$) states the amounts of whose spin-splitting are not known, the actual separations of the $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$ components of the normal state are not ascertainable. For the $^3\Pi_2$ state, which is lowest, the first level is that with $J'' = 2$, for the $^3\Pi_1$ state the first level is that with $J'' = 1$ and for the $^3\Pi_0$ state, which is highest, the first level is that with $J'' = 0$. The uncertainty arises because the case a spin-tripling probably amounts to several cm^{-1} , an amount of the same order of magnitude as the distance between the two or three lowest rotational levels with $J'' = 0, 1, 2, \dots$. It can be stated that the lines with excitation potential zero (probably the strongest interstellar lines if a detectable amount of C_2 exists in interstellar space) are either the $R_3(0)$, $R_2(1)$ or $R_1(2)$ lines, and probably the last of these three.

⁵⁴ Johnson, *Phil. Trans. Roy. Soc.*, **226**, 157, 1927.

⁵⁵ Shea, *Phys. Rev.*, **30**, 825, 1927.

⁵⁶ Jenkins and Wooldridge, *Phys. Rev.*, **53**, 137, 1938.

⁵⁷ Jevons, *Proc. Roy. Soc.*, **112**, 407, 1926.

⁵⁸ Jenkins, Roots and Mulliken, *Phys. Rev.*, **39**, 16, 1932.

⁵⁹ Jenkins and McKellar, *Phys. Rev.*, **42**, 464, 1932.

TABLE 3. BAND LINES ARISING FROM THE LOWEST STATES OF MOLECULES OTHER THAN HYDRIDES—*Continued*

Molecule	Electronic transition	Band	Line	Wave-length	Excitation potential in cm ⁻¹	Reference
BO (cont'd)	$^1\Pi, ^2\Sigma$	1,0	$Q_1(1) + ^oR_{12}(1)$	4037.42	3.54	
	$^1\Pi, ^2\Sigma$	1,0	$R_1(1)$	4036.29	3.54	
	$^1\Pi, ^2\Sigma$	1,0	$Q_2(1) + ^oP_{21}(1)$	4017.77	3.54	
	$^1\Pi, ^2\Sigma$	1,0	$R_2(1) + ^oQ_{21}(1)$	4017.08	3.54	
	$^1\Pi, ^2\Sigma$	1,0	$^sR_{21}(1)$	4015.89	3.54	
	$^1\Pi, ^2\Sigma$	2,0	$R_1(0)$	~3847.9	0.00	
	$^1\Pi, ^2\Sigma$	2,0	$^sR_{21}(0)$	~3829.4	0.00	
	$^1\Pi, ^2\Sigma$	2,0	$^oQ_{21}(0)$	~3830.9	0.00	
	$^1\Pi, ^2\Sigma$	2,0	$Q_1(1) + ^oR_{12}(1)$	~3848.5	3.54	
	$^1\Pi, ^2\Sigma$	2,0	$R_1(1)$	~3847.4	3.54	
	$^1\Pi, ^2\Sigma$	2,0	$Q_2(1) + ^oP_{21}(1)$	3830.46	3.54	
	$^1\Pi, ^2\Sigma$	2,0	$R_2(1) + ^oQ_{21}(1)$	3829.86	3.54	
	$^1\Pi, ^2\Sigma$	2,0	$^sR_{21}(1)$	~3828.9	3.54	
	$^1\Pi, ^2\Sigma$	3,0	$R_1(0)$	~3678.7	0.00	
	$^1\Pi, ^2\Sigma$	3,0	$^sR_{21}(0)$	~3661.8	0.00	
	$^1\Pi, ^2\Sigma$	3,0	$^oQ_{21}(0)$	~3662.4	0.00	
	$^1\Pi, ^2\Sigma$	3,0	$Q_1(1) + ^oR_{12}(1)$	~3679.2	3.54	
	$^1\Pi, ^2\Sigma$	3,0	$R_1(1)$	~3678.3	3.54	
	$^1\Pi, ^2\Sigma$	3,0	$Q_2(1) + ^oP_{21}(1)$	3662.72	3.54	
	$^1\Pi, ^2\Sigma$	3,0	$R_2(1) + ^oQ_{21}(1)$	3662.20	3.54	
	$^1\Pi, ^2\Sigma$	3,0	$^sR_{21}(1)$	3661.31	3.54	
N_2^+	$^2\Sigma, ^2\Sigma$	0,0	$R(0)$	3909.70	0.00	60
	$^2\Sigma, ^2\Sigma$	0,0	$R(1)$	3909.02	3.84	
	$^2\Sigma, ^2\Sigma$	0,0	$P(1)$	3910.93	3.84	
	$^2\Sigma, ^2\Sigma$	1,0	$R(0)$	~3577.9	0.00	
	$^2\Sigma, ^2\Sigma$	1,0	$R(1)$	~3577.3	3.84	
CO^+	$^1\Pi, ^2\Sigma$	1,0	$P(1)$	~3578.9	3.84	61
	$^1\Pi, ^2\Sigma$	3,0	<i>Several lines</i>	~4914.5	0.00 and 3.93	
	$^1\Pi, ^2\Sigma$	3,0	"	~4884	0.00 and 3.93	
	$^1\Pi, ^2\Sigma$	4,0	"	~4568.5	0.00 and 3.93	
	$^1\Pi, ^2\Sigma$	4,0	"	~4542.5	0.00 and 3.93	
	$^1\Pi, ^2\Sigma$	5,0	"	~4274	0.00 and 3.93	
	$^1\Pi, ^2\Sigma$	5,0	"	~4251	0.00 and 3.93	
	$^1\Pi, ^2\Sigma$	6,0	"	~4020	0.00 and 3.93	
	$^1\Pi, ^2\Sigma$	6,0	"	~3999.5	0.00 and 3.93	
	$^1\Pi, ^2\Sigma$	7,0	"	~3797	0.00 and 3.93	
NO^+	$^1\Pi, ^2\Sigma$	7,0	"	~3779.5	0.00 and 3.93	62, 63
	?	0,0?		~5999	0.0 and 3.8	
SiN	$^2\Sigma, ^2\Sigma$	0,0	$R(0)$	4124.6	0.00	64, 65
	$^2\Sigma, ^2\Sigma$	0,0	$R(1)$	4124.36	1.46	
	$^2\Sigma, ^2\Sigma$	0,0	$P(1)$	4125.1	1.46	
	$^2\Sigma, ^2\Sigma$	0,0	$R(2)$	4124.12	4.37	
	$^2\Sigma, ^2\Sigma$	0,0	$P(2)$	4125.34	4.37	
	$^2\Sigma, ^2\Sigma$	1,0	<i>The 5 above lines</i>	~3962	0.00 to 4.37	
	$^2\Sigma, ^2\Sigma$	2,0	"	~3816	0.00 to 4.37	
AlO	$^2\Sigma, ^2\Sigma$	0,0	$R(0)(1)(2), P(1)(2)$	4844.7	0.00 to 3.83	66
	$^2\Sigma, ^2\Sigma$	1,0	$R(0)(1)(2), P(1)(2)$	4650.2	0.00 to 3.83	

⁶⁰ Childs, *Proc. Roy. Soc.*, **137**, 641, 1932.⁶¹ Baldet, *Annales O. Ap. Paris*, **7**, 1926. (Baldet's vibrational assignments have since been revised to those given above).⁶² Duffieux and Grillet, *Comptes Rendus*, **202**, 937, 1936.⁶³ Jausseran, Grillet and Duffieux, *Comptes Rendus*, **205**, 39, 1937.⁶⁴ Jenkins and de Laszlo, *Proc. Roy. Soc.* **122**, 103, 1929.⁶⁵ Mulliken, *Phys. Rev.*, **26**, 319, 1925.⁶⁶ Pomeroy, *Phys. Rev.*, **29**, 59, 1927.

TABLE 3. BAND LINES ARISING FROM THE LOWEST STATES OF MOLECULES OTHER THAN HYDRIDES—Continued

Molecule	Electronic transition	Band	Line	Wave-length	Excitation potential in cm ⁻¹	Reference
Na ₂	¹ Π, ¹ Σ	1,0	About 13 lines centred at	4894.7	0.0 to 4.6	67, 68
	¹ Π, ¹ Σ	2,0	" "	4865.7	0.0 to 4.6	
	¹ Π, ¹ Σ	3,0	" "	4837.5	0.0 to 4.6	
	¹ Π, ¹ Σ	4,0	" "	4809.9	0.0 to 4.6	
	¹ Σ, ¹ Σ	4,0	About 9 lines centred at	6611.4	0.0 to 4.6	69
	¹ Σ, ¹ Σ	5,0	" "	6561.3	0.0 to 4.6	
	¹ Σ, ¹ Σ	6,0	" "	6513.4	0.0 to 4.6	
	¹ Σ, ¹ Σ	7,0	" "	6466.1	0.0 to 4.6	
	¹ Σ, ¹ Σ	8,0	" "	6419.1	0.0 to 4.6	
	¹ Σ, ¹ Σ	9,0	" "	6373.8	0.0 to 4.6	
TiO	³ Π, ³ Π	0,0	Some 9 lines centred at	~5169	0.00 to 3.20	70
	³ Π, ³ Π	1,0	" "	~4956	0.00 to 3.20	
	B, ³ Π	0,0	Several lines centred at	~5600	0.00 to 3.20	71
	³ Σ, ³ Π	0,0	" "	~7058	0.00 to 3.20	72
	³ Σ, ³ Π	1,0	" "	~6654	0.00 to 3.20	
	³ Σ, ³ Π	2,0	" "	~6297	0.00 to 3.20	
K ₂	¹ Σ, ¹ Σ	4,0	About 20 unresolved lines centred at	~4310.3	0.0 to 4.0	73
	¹ Σ, ¹ Σ	5,0	" "	~4299.4	0.0 to 4.0	
	¹ Σ, ¹ Σ	6,0	" "	~4288.6	0.0 to 4.0	
	¹ Σ, ¹ Σ	7,0	" "	~4277.9	0.0 to 4.0	
	¹ Σ, ¹ Σ	8,0	" "	~4267.3	0.0 to 4.0	
	¹ Π, ¹ Σ	0,0	About 25 unresolved lines centred at	~6505	0.0 to 4.0	74, 75
	¹ Π, ¹ Σ	1,0	" "	~6473.7	0.0 to 4.0	
	¹ Π, ¹ Σ	2,0	" "	~6443.2	0.0 to 4.0	
	¹ Π, ¹ Σ	3,0	" "	~6413	0.0 to 4.0	
	¹ Π, ¹ Σ	4,0	" "	~6383.7	0.0 to 4.0	
	¹ Σ, ¹ Σ	0,0	About 20 unresolved lines centred at	~8566.4	0.0 to 4.0	76
	¹ Σ, ¹ Σ	1,0	" "	~8515.8	0.0 to 4.0	
	¹ Σ, ¹ Σ	2,0	" "	~8468.3	0.0 to 4.0	
	¹ Σ, ¹ Σ	3,0	" "	~8418.3	0.0 to 4.0	
	¹ Σ, ¹ Σ	4,0	" "	~8370.7	0.0 to 4.0	
	¹ Σ, ¹ Σ	5,0	" "	~8322.0	0.0 to 4.0	
	¹ Σ, ¹ Σ	6,0	" "	~8275.5	0.0 to 4.0	
	¹ Σ, ¹ Σ	8,0	" "	~8186.5	0.0 to 4.0	
	¹ Σ, ¹ Σ	11,0	" "	~8054.8	0.0 to 4.0	
ZrO	³ Π, ³ Π	0,0	Numerous unresolved lines centred at	~4620	0 to 5	77, 78
	³ Π, ³ Π	1,0	" "	~4453	0 to 5	
	B, ³ Π	0,0	" "	~5552	0 to 5	
	³ Σ, ³ Π	0,0	" "	~6230	0 to 5	

⁶⁷ Fredrickson and Watson, *Phys. Rev.*, **32**, 223, 1928.⁶⁸ Loomis and Wood, *Phys. Rev.*, **32**, 223, 1928.⁶⁹ Fredrickson and Stannard, *Phys. Rev.*, **44**, 632, 1933.⁷⁰ Christy, *Phys. Rev.*, **33**, 701, 1929.⁷¹ Lowater, *Proc. Phys. Soc. London*, **41**, 557, 1929.⁷² Christy, *Ap. J.*, **70**, 1, 1929.⁷³ Yamamoto, *Japanese Journal of Physics*, **5**, 153, 1929.⁷⁴ Loomis, *Phys. Rev.*, **38**, 2153, 1931.⁷⁵ Loomis and Nusbaum, *Phys. Rev.*, **39**, 89, 1932.⁷⁶ Crane and Christy, *Phys. Rev.*, **36**, 421, 1930.⁷⁷ Lowater, *Proc. Phys. Soc. London*, **44**, 51, 1932.⁷⁸ Merrill, *Spectra of Long-Period Variable Stars*, University of Chicago Press, 1940, p. 38.

the lower state of an absorption line, at least for a molecule as effectively abundant as CN. Hence, for molecules heavier than CN, several states might be so populated and a correspondingly greater number of transitions leading to absorption lines take place. In general, lines arising from states up to about 5 cm^{-1} (0.0006 volts) above the lowest have been included for the molecules in Table 3. A column has been included in this table giving, where possible, the excitation potential of each line in cm^{-1} units. To obtain this quantity in the more familiar electron-volts, the value in cm^{-1} should be divided by 8066.0 . For some of the molecules in Tables 2 and 3, particularly the heavier ones, it was not possible for the laboratory investigator to measure the lines right up to the origin of the band. In such cases it was usually possible for the present purpose to extrapolate from the measured lines to obtain reasonably accurate values of the wave-lengths of the lines of interest near the band origin. It has been indicated in the tables where the wave-lengths are not exact but approximate.

It will be noted that Table 4, in which are listed the molecules whose band systems involving the normal state lie outside the astronomically observable spectral region, contains a number of very common and stable diatomic molecules. If CH and CN are present in interstellar space, it is almost certain that at least some of the molecules in Table 4 are present there. It is indeed unfortunate that we cannot further our knowledge of the constitution of the material in interstellar space by observing the wave-length regions where these bands occur. One borderline case is that of NO where a considerable

TABLE 4. COMMON DIATOMIC MOLECULES FOR WHICH THE KNOWN BAND SYSTEMS ARISING FROM THE NORMAL STATE LIE OUTSIDE THE ASTRONOMICALLY OBSERVABLE REGION

Molecule	Region of "resonance" bands
H ₂	<1100A
N ₂	<1500
CO.....	<2500
NO.....	<2300
O ₂ ⁺	<2600
O ₂	<2400*
SiO.....	<2500

*See statement in text concerning "atmospheric" bands of O₂.

part of two band systems, the β and γ bands, arising from the normal state, occur at wave-lengths greater than 3000A . However, in connection with interstellar lines, we are only interested in the $v', 0$ bands. The $0,0$ bands of these NO systems occur at wave-lengths $\lambda\lambda 2202$ and 2269 , respectively, shorter than $\lambda 3000$, so they and all the $v', 0$ bands, which are necessarily at wave-lengths shorter than the $0,0$ bands, could not be photographed in a stellar spectrum. The same is true for the Schumann-Runge system of O₂.

It is well known, too, that the far red atmospheric bands of O₂ originate on the ground state. These, however, correspond to a triplet-singlet "forbidden" transition,

and to magnetic dipole radiation, so only the very great path length of the earth's atmosphere makes their intensity appreciable. Unless the density of O_2 in interstellar space is much greater than is now considered likely, it is improbable that any line or lines of the atmospheric O_2 bands would occur as interstellar lines.

SECTION IV—DISCUSSION

For reference purposes, at the beginning of this section containing discussions of several points concerning interstellar lines, a list of all such absorption lines, discovered up to the present time, is assembled in Table 5. The table contains the wave-length of the line, the identity of the absorbing atom or molecule, and the name of

TABLE 5. ABSORPTION LINES OF INTERSTELLAR ORIGIN

Wave-length	Identification	Discoverer
3072.97A	Ti II	Dunham and Adams (1936)
3229.19	Ti II	Dunham and Adams (1936)
3241.99	Ti II	Dunham and Adams (1936)
3302.32	Na I	Miss Heger (1921)
3302.99	Na I	Miss Heger (1921)
3383.76	Ti II	Dunham and Adams (1936)
3719.94†	Fe I	Dunham and Adams (1941)
3859.92‡	Fe I	Dunham and Adams (1941)
3874.00	CN	Adams (1940)
3875.77†	CN	Adams (1941)
3874.61	CN	Adams (1939)
3878.77	CH	Adams (1940)
3886.39	CH	Adams (1940)
3890.23	CH	Adams (1940)
3933.67	Ca II	Hartmann (1904)
3934.29	NaH ?	Dunham (1937)
3968.47	Ca II	Hartmann (1904)
4226.73	Ca I	Dunham (1937)
4300.31	CH	Dunham and Adams (1937)
5889.95	Na I	Miss Heger (1919)
5895.92	Na I	Miss Heger (1919)
7664.91	K I	Dunham (1937)
7698.98	K I	Dunham (1937)
3579.04	CH ⁺ ?§	Adams (1940)
3745.33	CH ⁺	Adams (1940)
3957.74	CH ⁺	Adams and Dunham (1937)
4232.58	CH ⁺	Dunham and Adams (1937)
4430.6*		Merrill (1934)
5780.55*		Merrill (1934)
5797.13*		Merrill (1934)
6202.99*		Merrill and Wilson (1938)
6269.99*		Merrill and Wilson (1938)
6283.91*		Merrill (1934)
6613.9*		Merrill (1934)

See the footnote on page 271.

† (Added in proof). The detection of these Fe I lines has been very recently announced (*P.A.S.P.*, **53**, 341, 1941; also, cf. reference No. 9a, p. 236).

‡ This line was added some time after the paper was completed.

§ See footnote added in proof on p. 269.

* These lines are diffuse in character, not sharp as are all the others.

the discoverer, as well as the date of discovery. In the upper part of the table are presented the lines which have been identified, while the lower part contains those as yet unidentified. § It will be noted that the twenty-seven identified lines represent eight chemical elements. The presence of five of these, Na I, Ca I and Ca II, Ti II, Fe I, and K I, has been revealed by their atomic spectra. The other three, H, C, and N, whose "ultimate" atomic lines lie in the astronomically unobservable ultra-violet, have been detected by the molecular spectra of the compounds CH and CN. The wave-lengths in the upper section are laboratory values, while for the lower section they are necessarily those measured in stellar spectra. All the lines in Table 5 except those marked with an asterisk are very sharp compared with the stellar lines in the spectra of early type stars. However, the seven marked by an asterisk are not so, those in the red being somewhat diffuse (up to about 5 angstrom units in width), while the line at $\lambda 4430$ is extremely wide (some 40 angstrom units). To complete our compilation of data on interstellar lines, attention should be drawn to the emission lines of the H, N II, O II and O III interstellar atoms found by Struve and Elvey, and referred to on p. 253.

OBSERVATION OF THE SHARP MOLECULAR LINES

The diffuse lines and also the strongest of the sharp lines, those of Na I and Ca II, can be easily photographed, using the usual single-prism stellar spectrograph of moderate dispersion. However, all the others, because of their extreme narrowness and weakness, can be photographed only with a spectrograph of very high dispersion and resolving power. Attempts have been made to observe these lines with the most powerful form of our universal spectrograph at Victoria. This relatively powerful stellar spectrograph has three prisms, the dispersion and theoretical resolving power at $\lambda 3933$ being 5 Å/mm and almost 100,000, respectively. With this instrument, in the spectrum of ξ *Persei* (O7nk) the sharp CH line at $\lambda 4300.3$ could be detected, but not with ease, while in the spectrum of χ^2 *Orionis* (B2ssk) the line at $\lambda 3934.3$ was measurable. In the spectrum of ζ *Ophiuchi* (B0nnk) the CH line at $\lambda 3886.4$ was just barely discernable. As may be seen in Plate III of Adams' article¹, the last of these is extremely well defined on the Mount Wilson plates. On a Victoria spectrogram of H.D. 21389 (cA0) a line much sharper than the stellar lines was measured at $\lambda 3874.9$; since this wave-length depends on those of the *H* and *K* lines of Ca II, which in this star are blends, partly of stellar and partly of interstellar origin, the sharp line might well be the *R*(0) line of the $\lambda 3883$ CN band at $\lambda 3874.6$. The conclusion drawn from the attempts made at Victoria during the past year to photograph these sharp lines is that our best equipment has only barely enough dispersion and resolving power to enable their detection under the most favourable conditions, and not enough to render possible the satisfactory prosecution of a program of observation of these lines. Only with a spectrograph having dispersion and resolving power comparable to the Mount Wilson coude instrument (dispersion up to 2.9 Å/mm, theoretical resolving power something over 100,000 in the second order of the grating) can these faint sharp interstellar lines be satisfactorily photographed.

§ See footnote added in proof on p. 269.

THE "ROTATIONAL" TEMPERATURE OF INTERSTELLAR MOLECULES

In his study of diffuse matter in interstellar space, Eddington⁷⁹ derived, on three different concepts, the temperature of the material there. Considering first the average density of radiation in a region remote from any star, he found from the Stefan-Boltzmann Law, $E = aT^4$, that the effective temperature corresponding to this density was $3^{\circ}2K$. Radiation in interstellar space, being the integrated total radiation from many sources of different temperatures and intensities, certainly does not correspond to a Planckian distribution for any one temperature. Since it is richer in short-wave-length constituents than in long-wave-length radiation (relative to equilibrium radiation at the above low temperature), a body selectively absorbing the former will be effectively at a higher temperature than one selectively absorbing longer wave-lengths. This was pointed out by Fabry⁸⁰. Eddington went on to evaluate an equivalent temperature T_{λ} for each wave-length λ such that the actual density of radiation for wave-length λ is equal to equilibrium radiation at T_{λ} . Taking the same reasonable distribution of stars of different temperatures as Eddington did, and total radiation density of 10^{-12} ergs per cc., it is found that at wave-lengths $2000\text{\AA}$, 10μ and 100μ values of T_{λ} are $1750^{\circ}K$, $47^{\circ}K$, and $5^{\circ}K$, respectively. A third concept of temperature treated by Eddington was that which corresponded to the average kinetic energy of the electrons liberated from atoms in interstellar space, mainly by short-wave-length light from the hotter stars. In consideration of the fact that in this process the hotter stars play a predominating role and on the as yet observationally unjustified assumption that at very short wave-lengths the radiation of these stars follows a Planckian distribution, he estimated for such a temperature the value $10,000^{\circ}K$. The observations of Adams¹ on the molecular interstellar lines now allow us to compute a temperature for molecules in interstellar space, the "rotational" or "effective" temperature, which governs the population of the lowest rotational states of the molecules giving rise to the interstellar molecular lines. Such a temperature as this has the virtue that it depends upon more directly obtained observational data than the three previously mentioned, that is, on the relative intensities of the interstellar lines from the different rotational levels of a single molecule. It has the disadvantage that it is based upon the assumption of a distribution of molecules among these states corresponding to thermal equilibrium and it could be argued that, except perhaps for localized regions, such a distribution is not approximated for molecules in interstellar space. However, in the case of many laboratory sources of band spectra, including arcs and discharge tubes, sources where at first it was not expected from *a priori* considerations that a Maxwell-Boltzmann distribution of molecules among the rotational states would exist, it has been shown that such a type of distribution apparently does hold and so enables the determination for the source in question of a "rotational" temperature. While this may not be the same as the "translational" temperature of the source, it, at least, is a parameter of some value in that it serves to define the distribution of the molecules among the rotational states. Hence, in interstellar space a somewhat similar situation might exist, and in any case the "rotational" temperature found from the molecular lines for interstellar space will have its own, perhaps limited, significance, as have the three other "temperatures" mentioned above.

⁷⁹ *Internal Constitution of the Stars*, Cambridge University Press, 1926, Chapter XIII; *Proc. Roy. Soc.*, **111**, 424, 1926.

⁸⁰ *Ap. J.*, **45**, 269, 1917.

Assuming, as above stated, that a distribution of molecules corresponding to thermal equilibrium at absolute temperature T exists for molecules in the initial rotational states, the intensity I of an individual line in a band is given by the expression:—

$$I = C i e^{-E_r/kT}, \dots \dots \dots (2)$$

where C is a constant; i is the intensity factor which depends on the product of the transition probabilities by the statistical weights of the states concerned and which is exactly determinable as a function of the rotational quantum numbers J' and J'' for all common types of electronic transition; E_r is the rotational energy of the initial state and it is given with sufficient accuracy by the expression $B_v J(J+1) + \dots$, in which B_v is the chief rotational constant, equalling $h/8\pi^2 c I_v$, where I_v is the effective moment of inertia of the molecule in the vibrational state determined by v ; and k is the Boltzmann constant. When E_r is expressed in cm^{-1} units, this expression⁸¹ becomes,

$$I = C i e^{-B_v J(J+1) + \dots / 0.695 T} \dots \dots \dots (3)$$

Usually, the value of T for a band spectrum source is obtained by plotting the function of the measured intensities of numerous band lines, $\log(I/i)$, against $J(J+1)$. If thermal equilibrium holds among the molecules in the source, a straight line results, the slope of which immediately allows the evaluation of T . In the present case, since we have only two lines of the R branch of the $\lambda 3883$ CN band available, a thermal distribution cannot be demonstrated but must be assumed in order to evaluate T from equation (3). Dr. Adams has kindly communicated to the writer his estimate of the relative intensity, in the spectrum of ζ *Ophiuchi*, of the $\lambda 3874.62$, $R(0)$ interstellar line of the $\lambda 3883$ CN band and the $\lambda 3874.00$, $R(1)$ line, as 5 to 1. $B_0 J''(J''+1) + \dots$ has the values 0 and 3.78 cm^{-1} for the 0 and 1 rotational states and for the two lines $R(0)$ and $R(1)$ the values of the intensity factor i are, respectively, 2 and 4. Thus from (3) we find, for the region of space where the CN absorption takes place, the "rotational" temperature,

$$T = 2.3K.$$

If the estimate of the intensity of $R(0)/R(1)$ were off by 100 per cent, this value of the "rotational" temperature would not be changed greatly, $R(0)/R(1) = 2.5$ giving $T = 3.4K$ and $R(0)/R(1) = 10$ giving $T = 1.8K$. On the basis of the above temperature we can determine the expected ratio of intensity of the $R_2(1)$ line of the $\lambda 4315$ band of CH at $\lambda 4300.3$, which has been observed as an interstellar line, to that of the $R_1(1)$ line at $\lambda 4303.9$, arising from the upper component of the normal doublet rotational state of CH, 18 cm^{-1} above the lower component, which has not been observed as an interstellar line. At $2.3K$, the resulting intensity ratio for these absorption lines turns out to be about 40,000 to 1, and so it is not surprising that the $R_1(1)$ line has not been observed. It would indeed be interesting to find and identify interstellar lines due to other molecules as heavy as, or heavier than, CN and so to learn whether the population of their lower rotational levels corresponds to the same "rotational" temperature as that given by CN.

Before leaving the subject of the temperature of interstellar matter, the obvious point may be noted that the validity of the various "temperatures" discussed above will be greatly clarified as our knowledge of the physical state of the matter in interstellar

⁸¹ Cf. Reference No. 45, pp. 133ff.

space increases. At the present time much fine work in this field is being done⁸², utilizing the great body of observational data obtained since the classical theoretical treatment of the subject was presented by Eddington fifteen years ago. Concerning diatomic molecules, the main point so far disclosed, other than their presence in interstellar space, is that nearly all the molecules are in the lowest possible energy state. Above, this has been interpreted in terms of a "rotational" temperature. The more fundamental mechanistic and not surprising fact is, however, that the average time between successive receipts of rotational energy by interstellar molecules is apparently long compared to the time taken to release such energy.

THE UNIDENTIFIED SHARP INTERSTELLAR LINES*

It will be noted that in Table 5 there are listed eleven interstellar lines as yet unidentified. As pointed out earlier, it is very unlikely that these are due to any atoms or atomic ions in gaseous form. The identification of interstellar CH and CN encourages us to examine carefully any available evidence bearing upon the possible identification of any of these eleven lines with spectral features due to diatomic molecules. Let us consider first the four sharp lines at $\lambda\lambda 4232.58, 3957.74, 3745.33$ and 3579.04 . If these lines are due to a diatomic molecule, since they apparently have not other similar lines close to them (within one or two angstroms) they must be due to a molecule lighter than CN, or, more strictly, a molecule having a smaller moment of inertia than CN. Otherwise it is almost certain that a line or lines arising from the next to lowest rotational state would be found near them, analogous to the $\lambda 3874.00, R(1)$ line which Adams found accompanying the $\lambda 3874.61, R(0)$ line of the $\lambda 3883$ CN band. Most known diatomic molecules lighter than CN are hydrides, and so it is not unlikely that these four lines may be due to hydride molecules. A further clue to their identification has been noted by Adams⁸³, who has observed that the relative intensities of the $\lambda\lambda 4232.58, 3957.74$ and 3745.33 lines seem to behave in the same manner from one star to another. This suggests that they may have a common origin. Also, their spacing in wave-length (or frequency) units is such as to suggest that they may be due to the same molecule, being the lines from the lowest state to a rotational state of succeeding vibrational upper states. They would thus be corresponding lines from bands of a $v', 0$ progression. If we go further and make the reasonable assumption that they are "ultimate" lines of the $0, 0, 1, 0$, and $2, 0$ bands, we can immediately calculate with considerable accuracy for this hypothetical molecule the vibrational constants of the particular upper electronic state involved. If our above assumption were true, the difference in wave-numbers between these successive lines would be very close (within about 1 cm^{-1} or better) to the difference in energy between

⁸² e.g., Spitzer, *Ap. J.*, **93**, 369, 1941.

Stromgren, *Ap. J.*, **89**, 526, 1939.

Struve, reference No. 9a.

⁸³ Private communication.

* (Note added in proof) While this paper was in press Douglas and Hertzberg (*Ap. J.*, **94**, 381, 1941) succeeded in producing in the laboratory the spectrum of CH^+ . They found that the lines from the lowest state in the $0, 0, 1, 0$, and $2, 0$ bands in the CH^+ system, namely the $R(0)$ lines of these bands, occur at wave-lengths $\lambda\lambda 4232.57, 3957.71$, and 3745.30 . These wave-lengths agree almost perfectly with those of the three strongest lines discussed in this section. This remarkably fine piece of research done by Douglas and Hertzberg leaves no doubt as to the correctness of the assignment of these three lines to the CH^+ molecular ion. This result is in gratifying accord with the conclusion reached in this section of the paper, namely that the lines were all probably due to a diatomic hydride molecule. It will be interesting to compare the vibrational constants of the upper state of CH^+ , when they are published, with those obtained here. Incidentally, it would appear that there is a definite probability that the interstellar line at $\lambda 3579.04$ is due to the $R(0)$ line of the $3, 0$ band of this CH^+ system.

successive vibrational levels of the upper electronic state. These energy differences, ΔG_v , between successive vibrational states, are given in cm^{-1} units by the expression

$$\Delta G_{v'} = \omega'_e - 2x'_e \omega'_e (v' + \tfrac{1}{2}) + 3y'_e \omega'_e (v' + \tfrac{1}{2})^2 + \dots \quad (4)$$

where v' is the upper vibrational quantum number, ω'_e is the fundamental frequency for infinitesimal amplitude of vibration, and $x'_e \omega'_e$ and $y'_e \omega'_e$ are successive anharmonic vibrational coefficients ($\omega_e \gg x_e \omega_e \gg y_e \omega_e$). For example, the difference $\Delta G_{\frac{1}{2}}$ is the spacing between the 0 and 1 vibrational levels, $\Delta G_{\frac{3}{2}}$ between the 1 and 2, . . . etc. Thus from the frequency differences of the three lines and (4) we get

$$\begin{aligned} \Delta G'_{\frac{1}{2}} &= 1640.2 = \omega'_e - 2x'_e \omega'_e \\ \Delta G'_{\frac{3}{2}} &= 1432.5 = \omega'_e - 4x'_e \omega'_e \end{aligned}$$

from which

$$\begin{aligned} \omega'_e &= 1848 \text{ cm}^{-1} \\ x'_e \omega'_e &= 104 \text{ cm}^{-1}. \end{aligned}$$

If we further assume that the $\lambda 3579.04$ line is due to the 3,0 band of the same band system (its wave-length makes this plausible), we may solve also for $y'_e \omega'_e$, obtaining

$$\begin{aligned} \omega'_e &= 1863 \text{ cm}^{-1} \\ x'_e \omega'_e &= 115 \text{ cm}^{-1} \\ y'_e \omega'_e &= 2.6 \text{ cm}^{-1}. \end{aligned}$$

We have restricted the $v',0$ progression by assuming that it begins with the 0,0 band, but it is not impossible that the $\lambda 4232.58$ line might be due to a $v',0$ band where $v' = 1, 2, 3, 4, \dots$. However, if so, it is probable that the $(v' - 1), 0$ band would give rise to a line around $\lambda 4590$, and a sharp line of interstellar character has apparently not been observed near this wave-length. Consideration of the values of the vibrational constants estimated for this hypothetical diatomic molecule is instructive. By referring to a table of molecular constants⁸⁴ it is evident that the above values of ω_e are around the mean for nearly all the light molecules, including hydrides. However, $x_e \omega_e$ for essentially all light molecules except hydrides is about 10 or 15 cm^{-1} , whereas for many hydrides it is around 40 or 50 cm^{-1} , and in a few cases is 100 cm^{-1} or more, which is of the order of the values found above. In lists of the constants determined for the electronic states of molecules so far studied, there appear to be none which coincide with those derived above for our hypothetical molecule. Concluding the discussion of these sharp unidentified lines, the evidence presented in this paragraph, although perhaps not quite as direct as one could desire, indicates that if one or more diatomic molecules are responsible for them they are probably hydride molecules.

THE UNIDENTIFIED DIFFUSE INTERSTELLAR LINES

Considering, finally, Merrill's interstellar lines in the red and yellow spectral regions, while a careful search of available data on molecular spectra has yielded no coincidence thought to be significant, it is of interest to examine in the light of Adams' results on CN whether these unidentified diffuse features may possibly be due to diatomic molecules. Adams has shown that for CN, the $K'' = 1$ rotational level, 3.78 cm^{-1} above the lowest quantum level of the molecule, is appreciably populated and gives rise to an absorption line. For the $\lambda 3883$ CN band, the interstellar lines that would occur are $R(0)$, $R(1)$,

⁸⁴ Cf. Jevons, *Report on Band Spectra of Diatomic Molecules*, Published by the Physical Society, London, Appendix II, pp. 266ff, 1932.

and $P(1)$ at $\lambda\lambda 3874\cdot61$, $3874\cdot00$, and $3875\cdot77$, covering a spectral range of $1\cdot8\text{\AA}$ or 12 cm^{-1} . Incidentally, this $P(1)$ line at $\lambda 3875\cdot77$ should occur as an interstellar line with intensity half that of the $\lambda 3874\cdot00$, $R(1)$ line*. At $\lambda 6000$, 12 cm^{-1} would correspond to about $4\text{\AA}$, roughly the width of Merrill's diffuse lines. However, if these features were due to a molecule with a moment of inertia similar to that of CN, even if the electronic transition were more involved than the simple ${}^2\Sigma$, ${}^2\Sigma$ transition giving the violet CN bands and several more than three lines arose from the two lowest rotational states, it is probable that spectrograms would by now have shown the individual line structure. Considering a molecule with a somewhat greater moment of inertia than CN, say SiN for which $B_0'' = 0\cdot728\text{ cm}^{-1}$, we find that for $T = 2\cdot3K$ the three lowest levels would give rise to absorption lines of appreciable intensity. Thus, depending on the type of electronic transition, from five to about twelve or fifteen lines would appear, covering a region some 7 cm^{-1} in extent, which, at $\lambda 6000$, would correspond to almost $3\text{\AA}$. Going to a still heavier molecule, as heavy say as Na_2 for which $B_0'' = 0\cdot154\text{ cm}^{-1}$, it is found that, under the conditions assumed, as many as the six lowest rotational levels would act as lower states for the production of eleven or more lines covering only some 3 cm^{-1} or one angstrom unit. Therefore, if the "rotational" temperature of the region of interstellar space where the diffuse interstellar lines are produced is that found for CN and if the diffuse lines are caused by absorption by diatomic molecules, it would appear that the molecules concerned must be neither very light nor very heavy, but those having a moment of inertia of intermediate value (B_0'' from about $0\cdot5$ to $1\cdot0\text{ cm}^{-1}$). Absorption by molecules with lower moment of inertia should be easily resolvable into component band lines, while that due to molecules with a greater moment of inertia would be considerably narrower than the observed widths of the interstellar lines. If the rotational temperature of the molecular matter in the space where these lines are produced should be greater than that considered above (as it probably is in the neighbourhood of stars), the possibility of the heavier molecules causing the lines would be considerably enhanced. The symmetry or lack of it of apparent diffuse lines caused by molecular absorption as above would depend on the relative values of the constants B_u for the upper and lower states concerned. Generally speaking, one would expect the features to be fairly symmetrical, as the observed interstellar lines are found to be. In any case, if definite structure could be observationally revealed for one or more of these diffuse lines, it would doubtless aid greatly in solving the problem of their chemical origin. It is extremely desirable that these features be observed with the highest practicable spectrographic dispersion and resolving power.

The very wide interstellar absorption centred at $\lambda 4430$ and extending twenty angstrom units on each side of this wave-length would appear to be definitely too extensive to be caused by gaseous interstellar diatomic molecules, unless caused by some peculiar predissociation process or by some homonuclear molecule, should the assumption discussed in the footnote on p. 256 not hold true. The suggestion by Beals and Blanchet that it may be due to absorption by solid particles would appear to be as good as any available at present. Indeed, the strong correlation pointed out by Merrill and Wilson between the intensities of the diffuse interstellar lines in the red, and colour excess caused doubtless by small solid particles with diameters of the order of the wave-length of visible light,

*In June, 1941, Dr. W. S. Adams informed the writer in a letter that he had succeeded in detecting with certainty this faint $P(1)$ line of the $0, 0$ CN band at $\lambda 3875\cdot77$, on spectra of ζ *Ophiuchi* taken with the coude spectrograph at Mount Wilson Observatory.

cannot be disregarded, and these lines, as Merrill and Wilson indicate, may be due to absorption by solid particles rather than molecular gases associated with the dust. However, present data on selective absorption by solids are very meagre and further examination of this phase of the problem of identification must await the development of theoretical and laboratory studies of selective absorption by solid matter and particles at low temperature.

In conclusion, the writer takes pleasure in acknowledging his appreciation of the kind co-operation of Dr. Walter S. Adams, Director of the Mount Wilson Observatory, in making available various observational results in advance of their publication.

DOMINION ASTROPHYSICAL OBSERVATORY

Victoria, B.C.

March, 1941.