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The Interstellar Line Spectrum of Zeta Ophiuchi

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The optical interstellar lines in ζ Oph are double (at —15, —29 km/sec) on ordinary spectrograms. The stronger component at —15 km/sec has been analyzed to obtain homogeneous data on the atomic and molecular concentrations in a specific interstellar volume. A curve of growth study yielded N, the total number of absorbers cm^{-2} for NaI, CaII, KI, CH and CN (and CH^+ when an absolute f-value becomes available). Upper limits are set on CaI, FeI, TiI, TiII, and the diatomic molecules OH, NH, MgH, SiH and CO^+. Correction of the atomic data for ionization was performed by evaluating the photoionization and recombination coefficients in the combined radiation field of ζ Oph (based on a line-blanketed photospheric model by Hickok and Morton) and that of the galaxy. Reduction of the N's to concentrations n (in cm^{-3}) was based on a model for the distribution of interstellar material between ζ Oph and the sun, beginning with an HII region of $n_e = 3$ cm^{-3} centered on the star. It was argued that the —15 km/sec spectrum must largely be formed in a dense HI region which lies somewhere between 15 and 50 pc from the star, and is succeeded by a tenuous HI region of $n(\mathrm{H}) \approx 0.1$ cm^{-3} extending to the sun. The properties of the dense HI region follow if the Na/H abundance in that cloud is equal to the solar-system value, as seems probable. On this basis together with a value of N(HI) obtained by Stecher from a rocket observation of interstellar Lα, the density derived for this HI layer is $n(\mathrm{H}) = 500$ to 900 cm^{-3} depending upon the distance from ζ Oph, while the thickness is about 0.15 pc. The abundance of K in this layer is normal, but Ca is deficient by about a factor 1400, and Ti by at least 100. Interstellar LiI and BeII lines are not detected in ζ Oph, but the observational thresholds are high; the upper limit on Li corresponds to 9 times its abundance in chondrites, while that for Be is 4—6 times the chondritic value. There is thus no evidence for interstellar Be depletion. At the high densities obtained for the HI layer, it is possible that the formation of diatomic molecules by 2-body radiative recombination proceeds at a significant rate. The coefficients of the Bates-Spitzer theory for CH, CH^+ formation have been modified to fit the circumstances at ζ Oph, and it appears that instead of a rate of molecule formation too small to fit the observations by a factor of about 10^3 as found by Bates and Spitzer, the discrepancy for CH is now reduced to about 30—40. The fact that the densities of NH and OH in front of ζ Oph are low with respect to $CH + CH^+$ and CN is expected if the 2-body process is dominant, but not if the molecules are formed by exchange reactions on graphite surfaces. Despite specific search, none of the accessible triatomic molecules that might be progenitors of the observed CN have been found.

1. Introduction

The interstellar absorption lines become stronger in more distant stars as the result of superposition of an increasing number of interstellar clouds. When the multiple structure is resolvable, it often differs among lines of different elements, demonstrating that there are physical differences between clouds. The analysis of such lines that are not resolved must result in some kind of average information which, conceivably, might not apply to the average individual cloud. For this reason there is justification for studying in detail one interstellar spectrum that is as simple as possible, wherein the very minimum of clouds overlap.

Another reason is that there is not now available a set of homogeneous data on molecular and atomic abundances in one specific region of the interstellar medium, upon which calculations of molecular and ionic processes might with confidence be based. The nearest approach to such a body of data is that resulting from the study by STRÖMGREN (1948) as modified by SEATON (1951), of the interstellar atomic lines in χ^2 Orionis, but those results are now susceptible to some improvement. Although most of the known interstellar lines in the optical region had been found by W. S. ADAMS, T. DUNHAM, and their predecessors 25 years or more ago, accurate spectrophotometric data on the faint lines are rather sparse, and hence there is no way to take advantage properly of the large body of new or more accurate f-values, both atomic and molecular, that are now available. Furthermore there is some value in setting firm upper limits on the abundances of undetected interstellar ions and free radicals, some of which are of significance even in their absence (as in the cases of Be II and NH).

There were in addition some more special motives for the present study, particularly the question of the Li abundance in interstellar clouds that contain T Tauri stars, and matters having to do with the diffuse interstellar bands; the latter however will not be discussed here.

For these purposes, the most suitable star accessible from California is ζ Ophiuchi[1], which despite its brightness and only moderate reddening ($E_{B-V} = +0.32$), exhibits a rather strong interstellar line spectrum with a particularly fine showing of molecular lines. From the fairly high latitude, one expects that the line of sight to ζ Oph passes through a minimum number of intervening clouds and therefore that the observed interstellar lines may all originate in a single volume. As will be seen however, this aim of finding a star with a suitably strong yet uncomplicated interstellar line spectrum has been achieved only imperfectly.

A further advantage of ζ Oph is that, due to the concentration of the interstellar material in the vicinity of the star, the stellar radiation field largely dominates the ionization equilibrium, so that in ionization calcula-

[1] = HD 149757. $\alpha(1900) = 16^h31^m\!.6$, $\delta(1900) = -10°22'$; $l^{II} = 6\overset{\circ}{.}3$, $b^{II} = +23\overset{\circ}{.}6$. V = 2.57, B—V = +0.02, U—B = —0.84; MK type O 9.5 V. The stellar lines are very broad due to rotation with $v \sin i \approx 250$ km/sec, so there is no confusion between stellar and interstellar features.

tions there is less dependence on the general galactic field with its uncertainty arising from the imperfectly-known law of interstellar extinction in the far ultraviolet.

The spectroscopic observations were all made with the coudé spectrograph, 120-inch reflector. The dispersions were 1.3 and 2.0 Å/mm in the photographic region and the ultraviolet, 4.1 Å/mm in the yellow-red, and 16 Å/mm in the infrared. Two special products of these observations have already been published: the equivalent widths of the interstellar CN lines have been discussed by FIELD and HITCHCOCK (1966), and the C^{12}/C^{13} abundance ratio inferred from the CH^+ $\lambda 4232$ line has been reported by AUGASON and HERBIG (1967).

According to BLAAUW (1961) the space motion of ζ Oph indicates an origin for the star in the northern part of the Sco-Cen association about 1.1×10^6 years ago. The region of ζ Oph and the area to the south whence it came is strewn with irregular patches and lanes of dark material. In Hα light, ζ Oph is seen to be surrounded by a circular emission nebulosity about 5° in radius (SHARPLESS and OSTERBROCK, 1952; MORGAN, STRÖMGREN and JOHNSON, 1955) against which some of the foreground dark material is seen in projection. This emission nebulosity is presumably material of the Sco-Oph clouds that temporarily lies within the Strömgren radius of ζ Oph in its northward motion. The cross-motion of the star is such as to carry it the angular radius of the nebulosity in about 7×10^5 years.

At conventional dispersions (2—4 Å/mm), the Na I and Ca II interstellar lines in ζ Oph appear double, with the stronger component at about —15 km/sec and the weaker at about —29 km/sec. (More precise velocities are given in Table 1.) I am indebted to Drs. C. R. and B. T. LYNDS for sending me enlargements of two spectrograms of the Na I $\lambda 5889$ line in ζ Oph taken with the Kitt Peak solar telescope and the instrumentation of LIVINGSTON and LYNDS (1964), at a dispersion of 0.2 Å/mm. Dr. L. M. HOBBS also very kindly furnished a tracing of the same line obtained with his pressure-scanning Fabry-Perot interferometer at the Lick 120-inch reflector (HOBBS, 1965) and a resolution of 6×10^5. At these resolutions, structure can be detected in the bottom of the strongest component at —15 km/sec, and at least 4 other weak resolved lines are seen, near —9, —26, —28, and —33 km/sec. The present study is devoted entirely to the set of lines at —15 km/sec, but it is probable that the weak, blended component at —9 km/sec contributed slightly to the measured equivalent widths. As will be shown later, there is reason to believe that the —15 km/sec spectrum is formed predominantly in foreground H I material, not in the bright H II region around ζ Oph.

Table 1. *The occurrence of the known interstellar lines in ζ Ophiuchi*[1]

Laboratory or *predicted λ*	Identification	Reference to: Lab λ	Reference to: Earlier work	Mean measured radial velocity (km/sec) [standard deviation (km/sec)/number of plates] In −29 km/sec cloud	Mean measured radial velocity In −15 km/sec cloud	Measured equivalent width (mÅ) on (n) plates of ζ Oph In −29 km/sec cloud	Measured equivalent width In −15 km/sec cloud	Note
3072.971	Ti II	1	8	—	—	<3.	<3.	
3137.53	CH	3	9	—	−13.0:[2.8/3]	—	4.0 (2)	
3143.15	CH	3	9	—	−12.5 [0.7/5]	—	7.4 (2)	
3146.01	CH	3	9	—	−15.4 [0.8/4]	—	5.0 (2)	
3229.193	Ti II	1	8	p	—	<3.	<3.	
3241.986	Ti II	1	8	−26.5 [1.8/3]	—	5.9 (1)	<3.	
3302.375	Na I	2	—	—	−14.4 [0.4/5]	—	28.7 (4)	
3302.987	Na I	2	—	−29.6:[2.8/2]	−14.4 [0.2/5]	—	22.3 (4)	
3383.761	Ti II	1	8	−27.3 [1.6/5]	—	6.9 (3)	<3.	
3440.610	Fe I	1	—	—	—	—	<3.	15
3447.075	CH^+	4	—	—	p	—	1—2:	14
3579.020	CH^+	4	4, 10	—	p	—	3.7 (2)	
3719.935	Fe I	1	11	—	—	—	<3.	
3745.310	CH^+	5	10	—	−15.1 [1.0/7]	—	7.2 (6)	
3859.913	Fe I	1	11	—	—	—	<3.	
3873.998	CN	7	12, 10	—	−13.8 [1.0/4]	—	3.4 (6)	
3874.608	CN	7	12, 10	—	−14.8 [0.4/6]	—	9.2 (6)	19
3875.763	CN	7	12, 10	—	−14.9 [1.1/3]	—	≦2. (5)	
3878.768	CH	6	12, 10	—	−13.3 [— /1]	—	3.: (1)	
3886.410	CH	6	12, 10	—	−14.4 [0.5/4]	—	5.9 (5)	
3890.213	CH	6	12, 10	—	−14.3 [0.3/3]	—	5.6 (5)	
3933.664	Ca II	1	—	−29.0 [0.3/6]	−15.0 [0.6/6]	10.1 (5)	34.2 (5)	18
3957.700	CH^+	5	13	—	−15.4 [0.4/6]	—	13.3 (6)	16
3968.470	Ca II	1	—	−28.0 [1.1/4]	−14.2 [0.3/6]	5.4 (5)	21.3 (6)	18
4226.728	Ca I	1	13	—	—	—	<3.	
4232.539	CH^+	5	13	—	−14.0 [0.7/6]	—	27.4 (3)	16
4300.321	CH	6	12, 10	—	−14.6 [0.4/5]	—	20.5 (2)	19
5889.953	Na I	1	—	−27.3 [— /1]	−15.1 [0.4/7]	p	239. (2)	
5895.923	Na I	1	—	—	−15.0 [0.3/7]	—	189. (2)	
7664.907	K I	1	13	—	p	—	p	17
7698.979	K I	1	13	—	−15.9 [1.0/4]	—	97. (3)	

[1] A p indicates that the line is present but was not measured.

Notes to Table 1

1. Revised multiplet table.
2. THACKERAY (1949)
3. McKELLAR (1940b)
4. DOUGLAS and MORTON (1960)
5. DOUGLAS and HERZBERG (1942)
6. MOORE and BROIDA (1959)
7. JENKINS and WOOLDRIDGE (1937)
8. DUNHAM and ADAMS (1937); DUNHAM (1937)
9. SPITZER and FIELD (1955); FEAST (1955); McKELLAR and RICHARDSON (1955); HERBIG (1960)
10. ADAMS (1941)
11. DUNHAM and ADAMS (1941)
12. McKELLAR (1940a, 1941)
13. DUNHAM (1937)
14. An exceedingly faint line, visible on only 3 of the best 2.0-Å/mm plates of ζ Oph, was measured at 3446.92 Å. Allowance for a cloud velocity of -14.6 km/sec corrects this to 3447.09 Å, which is very near the wavelength 3447.075 Å predicted for the 4—0, $R(0)$, line of CH^+ by DOUGLAS and MORTON (1960).
15. This line has been suspected in several stars in which interstellar Fe I is observed; it is not seen in ζ Oph.
16. WILSON (1948) measured $W^{(\lambda)} = 12 \pm 2$ and 16 ± 2 mÅ for CH^+ $\lambda\lambda$3957, 4232 respectively on two of ADAMS' 2.9-Å/mm plates of ζ Oph.
17. KI λ7664.91 is ordinarily masked by the terrestrial O_2 line at 7664.87 Å. The interstellar line can be seen separately in ζ Oph during the spring months, when the Doppler effect of the earth's orbital motion shifts the lines out of coincidence.
18. ADAMS (1949) gives radial velocities for the two components of the Ca II lines, corrected to the laboratory wavelengths of col. 1, of -29.0 and -14.6 km/sec.
19. DUNHAM (1941) gives $W^{(\lambda)} = 6$ and 14 mÅ for the interstellar lines CN λ3874.608 and CH λ4300 respectively in ζ Oph.

2. Curve of Growth Analysis

We proceed in general along the line of the method described by STRÖMGREN (1948) in which the equivalent width of each line in units of the appropriate Doppler constant, $\log W^{(\lambda)}/b^{(\lambda)}$, is expressed in terms of the optical depth in the line center

$$\log \tau_0 = \log N \frac{\pi^{1/2} e^2}{m c^2} f \frac{\lambda^2}{b^{(\lambda)}}, \tag{1}$$

where N is the number of absorbers cm^{-2} column, f is the oscillator strength, λ is the wavelength, and e, m, and c are the usual physical constants. A superscript (λ) indicates that that quantity is expressed in wavelength units. In the case of thermal motion,

$$b^{(\lambda)} = \frac{\lambda}{c} \left(\frac{2kT}{A m_0}\right)^{1/2}, \tag{2}$$

k being the Boltzmann constant, T the temperature, and $A m_0$ the mass of the atom; in velocity units,

$$b = b^{(\lambda)} \frac{c}{\lambda_0} \tag{3}$$

STRÖMGREN has calculated $\log W^{(\lambda)}/b^{(\lambda)}$ as a function of $\log \tau_0$ by numerical integration over the appropriate expression for the atomic absorption coefficient. For very strong lines broadened by radiation damping, the ratio a of the radiation damping parameter to the Doppler width enters, but for the strongest line considered here (Na I λ5889, with $\log \tau_0 = +2.1$) the effect is negligible. The fit of the 4 Na I lines to STRÖMGREN's theoretical curve gives[2] for the —15 km/sec spectrum N(Na I) $= 4.90 \times 10^{13}$ cm^{-2}, b(Na I) $= 2.43$ km/sec.

The doublet ratio method must be used for Ca II, because the next members of the $^2S - n^2P^\circ$ series following H and K lie at 1650 Å, beyond the atmospheric cutoff. The method is more trustworthy for Ca II than in the case of Na I however, since the Ca II lines are much weaker; b(Ca II) will be less well determined on that account. The result is N(Ca II) $= 5.4 \times 10^{11}$, b(Ca II) $= 1.54$ km/sec. The scatter of the measurements of $W^{(\lambda)}$ for these Ca II lines on individual spectrograms indicates a probable error in the mean of ± 0.8 mÅ, which corresponds to probable errors in $\log N$(Ca II) of ± 0.05 and in b(Ca II) of ± 0.3 km/sec.

The other lines in the —15 km/sec spectrum are too weak to determine b, but the N's read from the curve of growth[3] are listed in Table 3; unless otherwise noted, they have been obtained with the assumption that

Table 2. *Collection of atomic f-values*

Ion	λ	f	Reference
Na I	3302.375	0.0047	ALLEN (1963)
	3302.987	0.0094	
	5889.953	0.67	
	5895.923	0.33	
Ca I	4226.728	1.49	OSTROVSKI and PENKIN (1961)
Fe I	3719.935	0.053	CORLISS and WARNER (1966)
Ti I	3341.88	0.28	[a]
	3635.46	0.16	
Ti II	3241.984	0.16	WARNER (1967)
	3383.761	0.26	
K I	4044.145	0.01	HEAVENS (1961)
	7698.979	0.35	
Li I	6707.761	0.53	ALLEN (1963)
	6707.912	0.26	
Be II	3131.06	0.18	ALLEN (1963)
	3130.42	0.35	

[a] The f-values of CORLISS and BOZMAN (1962) have been scaled to agree with those determined by REINKE (1967).

[2] As emphasized by STRÖMGREN, the "doublet ratio" method is untrustworthy for such strong lines on account of the effect of small errors in the equivalent widths. In this case, $D_2/D_1 = 1.265$, which leads to N(Na I) $= 4.0 \times 10^{12}$, b(Na I) $= 4.2$ km/sec, values that are in poor agreement with those from all 4 Na I lines considered together.

[3] In this and following Tables, quantities of the form A $\times$ 10$^{\mathrm{B}}$ are printed as A (B).

Table 3. *Abundances from interstellar lines of the —15 km/sec cloud, ζ Oph*

Atom	Number of lines	N (atoms cm^{-2})	b (km/sec)	Remarks
Na I	4	4.9 (+13)	2.4	
Ca I	(1)	<1.3 (+10)	—	
Ca II	2	5.4 (+11)	1.5	
Fe I	(1)	<5.0 (+11)	—	
K I { λ 7698:	1	8.0 (+11)	—	Assumed: $b = 2.4$ km/sec
K I { λ 4044:	(1)	<2.0 (+12)	—	$W^{(\lambda)}$ (λ 4044) < 3 mÅ
Ti I	(2)	<1.1 (+11)	—	
Ti II	(2)	<1.6 (+11)	—	
Li I	(1)	<1.9 (+10)	—	Sec. 5
Be II	(2)	<8.3 (+10)	—	Sec. 5

Molecule	System	Number of lines	N (molecules cm^{-2})	b (km/sec)	Remarks
CH$^+$	$A^1\Pi - X^1\Sigma$	5	—	0.85	$Nf_{el} = 5.7$ (+11)
CH	$A^2\Delta - X^2\Pi$	1	3.8 (+13)	—	Table 8
	$B^2\Sigma^- - X^2\Pi$	3	4.5 (+13)	—	
	$C^2\Sigma^+ - X^2\Pi$	3	—	—	$Nf_{el} = 7.3$ (+10)
CN	$B^2\Sigma^+ - X^2\Sigma^+$	1	4.8 (+12)	—	$N'' = 0$; Table 9
		1	3.9 (+12)	—	$N'' = 1$
		1	≦2.6: (+12)	—	$N'' = 1$
OH	$A^2\Sigma - X^2\Pi_i$	(1)	<8.3 (+13)	—	Table 10
NH	$A^3\Pi_i - X^3\Sigma^-$	(1)	<7.4 (+12)	—	Table 11
MgH	$A^2\Pi - X^2\Sigma^+$	(3)	<4.3 (+12) ?	—	Table 12
SiH	$A^2\Delta - X^2\Pi$	(1)	<5.6 (+12) ?	—	Table 12
CO$^+$	$A^2\Pi_i - X^2\Sigma^+$	(3)	<3.5 (+13)	—	Table 12

Table 4. *Resonance atomic lines specifically sought in ζ Oph, with negative results* [a]

Al I	3944.01	Mg I	4571.10
Ba I	5535.48	Mn I	4030.76
Ba II	4554.03	Ni I	3624.73
Co I	3474.02	[O I]	6300.30
Cr I	4254.35	Sc I	3907.49
	4274.80		4020.40
Cu I	3247.54	Sc II	3580.94
	3273.96		3642.79
Ga I	4032.98	Sr I	4607.33
Gd I	3684.13	Sr II	4077.71
	4327.12		4215.52
Gd II	3813.97	V I	3818.24
	3850.97		3855.37
In I	4101.76	Y I	4077.38
La I	3574.43		4142.85
	4187.32	Y II	3633.12
La II	4086.72		

[a] Aside from the cases of Ti I, Ti II, Li I, and Be II which are discussed in the text, the upper limits on all lines are about $W^{(\lambda)} = 3$ mÅ except for those having $\lambda > 5000$ Å, for which $W^{(\lambda)} = 5$ mÅ.

$b = 1.5$ km/sec. In the limit as $\tau_0 \to 0$,

$$\log \frac{W^{(\lambda)}}{b^{(\lambda)}} \to \log \tau_0 + \log \pi^{1/2} \tag{4}$$

and eq. (4) can be written

$$N = 1.130 \times 10^{20} \frac{W_A^{(\lambda)}}{\lambda_A^2 f} \tag{5}$$

where $W_A^{(\lambda)}$ and λ_A are in angstroms.

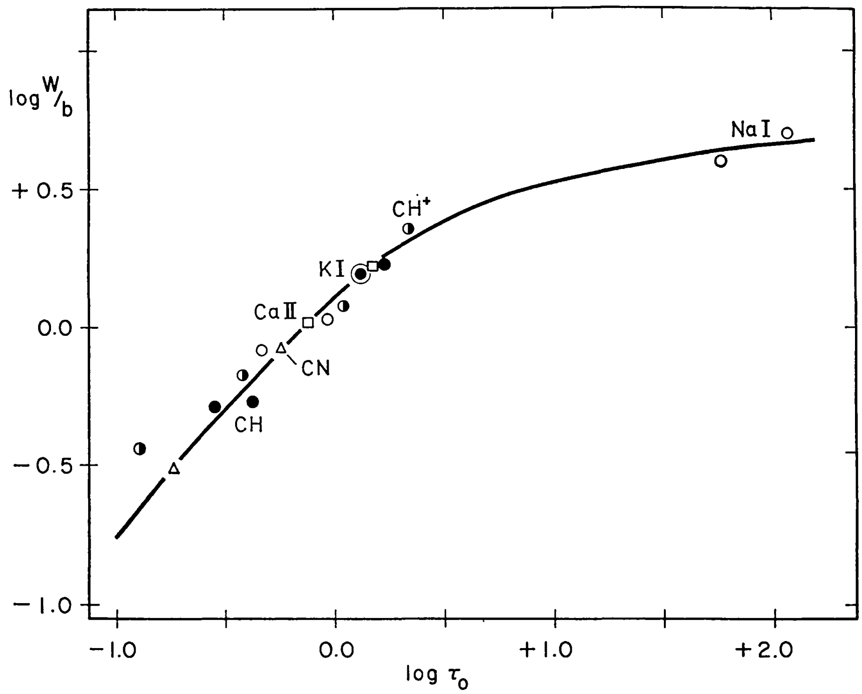

Fig. 1. The solid line is the theoretical interstellar curve of growth for zero damping calculated by Strömgren (1948). W is the equivalent width, b is the appropriate Doppler width, and τ_0 is the optical depth at the line center. The points represent individual lines in the —15 km/sec interstellar spectrum at ζ Ophiuchi, fitted to the curve with the Doppler widths and abundances given in Table 3. As indicated, open circles represent lines of Na I, filled circles CH, etc. Several very weak molecular lines having uncertain equivalent widths are not plotted

The interstellar Ti II lines are fairly strong in the —29 km/sec spectrum of ζ Oph, but they cannot be seen at —15 km/sec. Attention should be called to the fact that the upper limit thus set on N(Ti II) in Table 3 is based on modern f-values (Table 2). The discussions of the Ti II abundance in the interstellar spectrum of χ^2 Ori by Strömgren (1948) and Seaton (1951) were based on f-values about 60 times smaller than those used here, and so for compatibility, the N(Ti II) values published for χ^2 Ori should be lowered by the same factor.

Interstellar Fe I was not found in either set of lines in ζ Oph, although it is present weakly in the interstellar spectrum of the Be star χ Oph, some 7° away and reddened to $E_{B-V} = +0.53$ (GARRISON, 1967) by material of the same Sco-Oph dark clouds. The resonance lines of a number of other ions were sought in ζ Oph, with negative results. In some cases (such as Mg I λ4571 and [O I] λ6300) the line was not expected to be detectable, but a list of all the ions and wavelengths examined is given in Table 4, in case of possible future usefulness. The curve of growth is shown in Fig. 1, with all but the weakest lines plotted.

3. The Atomic Abundances

The presence of a H II region surrounding ζ Oph suggests that material in the ionized volume may contribute significantly to the interstellar line strength, because the high electron density due to H ionization depresses the level of ionization of elements such as Na and Ca, thus enhancing the lines of Na I and Ca II. In the case of Na, which in both H I and H II regions is predominantly once-ionized, the Na I concentration in a H II region is increased over that in a H I region of the same total density by a factor of approximately $n_e(\mathrm{H\,II}) \cdot (\Gamma/\alpha\,[\mathrm{H\,II}])^{-1}/n_e(\mathrm{H\,I}) \cdot (\Gamma/\alpha\,[\mathrm{H\,I}])^{-1}$, for equal Na concentrations. Here, Γ/α is the appropriate value of the right-hand side of the STRÖMGREN ionization equation (see below). In the case of Na exposed to the general galactic radiation field, this factor is about 50. Nevertheless, there are good reasons for believing that at least the —15 km/sec component of the interstellar lines in ζ Oph is predominantly formed in a H I region. These reasons are as follows:

1. This pattern of a strong interstellar Ca II line near zero velocity in the local standard of rest, accompanied by a weaker component about 15 km/sec shortward, is shown by a number of stars in this general direction, including ζ and χ Oph, 1 Sco, λ Lib observed by ADAMS (1949), and also 2 Sco, 22 Sco and δ Sco (HERBIG, unpublished). These stars are distributed over an area of the sky about 15° across. Of these only the earliest, ζ Oph, is involved in an H II region. Clearly, this line pattern is characteristic of the whole area and is not sensibly altered in ζ Oph by the presence of that H II region. Thus the lines must be formed in a very extensive foreground layer which in the absence of any general source of ionizing radiation is presumed to be an H I region.

2. A special series of scans of the 21-cm H I line on an east-west line extending 7° on either side of ζ Oph were very kindly made at my request by Dr. W. E. HOWARD with the 300-foot telescope at Green Bank, which has a beamwidth of 10′ at this frequency. The 21-cm profile along this line is single, somewhat steeper on the side toward negative velocities,

and has a peak velocity of —12.7 km/sec[4] at the position of ζ Oph. This peak must be identified with the stronger set of optical absorption lines at —15 km/sec. The same 21-cm structure, with peak velocity ranging between —10.5 and —12.9 km/sec, is the dominant feature along the entire 14° covered by these observations. This fact demonstrates that the optical counterparts of this 21-cm line must also originate in an H I region which covers a very extensive region of the sky, larger than the H II region around the star.

3. If the observed Na I lines were produced in a H II region, then the interstellar Na/H abundance ratio must be substantially higher than the solar system value. The reasoning is as follows. If n always denotes the concentration of particles cm^{-3} and N the total number cm^{-2}, then in an H II region

$$n(\mathrm{Na\,I}) = n(\mathrm{Na})\, n(\mathrm{H})\, (\Gamma/\alpha)^{-1}, \qquad (6)$$

where we take $n(\mathrm{Na}) \approx n(\mathrm{Na\,II})$, and $n_e = n(\mathrm{H})$. The solar system value is $n(\mathrm{Na})/n(\mathrm{H}) = 2.4 \times 10^{-6}$ (CAMERON, 1967), so

$$N(\mathrm{Na\,I}) = 7.4 \times 10^{12}\, \mathfrak{E}(\Gamma/\alpha)^{-1}, \qquad (7)$$

where $\mathfrak{E}$ is the emission measure in cm^{-6} pc. Calculations to be described later indicate that the value of Γ/α for Na I is about 600 at 10 pc from ζ Oph. There is no optical determination of $\mathfrak{E}$ for the ζ Oph H II region[5], but the feature is apparently present as a perturbation of one contour line of the 400 Mc/s continuum survey of SEEGER, WESTERHOUT, CONWAY and HOEKEMA (1965). As entry No. 83 in the catalogue of sources compiled by DAVIS, GELATO-VOLDERS and WESTERHOUT (1965) the feature is assigned dimensions of 4° × 5° and a flux density of 165: × 10^{-26} Wm^{-2} (c/s)$^{-1}$. These data can be converted into a value of $\mathfrak{E}$ provided that the source is thermal and optically thin. The latter is certainly so, and the first is assumed. From the relationships given by WESTERHOUT (1958) and with the assumption that $T_e = 10^4$ °K, one finds that $\mathfrak{E} = 350$. If the optical radius of 5° is used in this calculation rather than the rather uncertain radio dimensions, $\mathfrak{E} = 70$. From the first value and eq. (7), one obtains

$$N(\mathrm{Na\,I}) = 4.3 \times 10^{12}\ \mathrm{cm}^{-2},$$

yet the observations give

$$N(\mathrm{Na\,I}) = 4.9 \times 10^{13}\ \mathrm{cm}^{-2}.$$

[4] This velocity is +1.3 km/sec, referred to the local standard of rest. The wing on the side toward positive velocity may be produced by an unresolved component associated with the faint Na I line noted at a heliocentric velocity of —9 km/sec.

[5] The value of $\mathfrak{E} \approx 500$ quoted by SHARPLESS and OSTERBROCK (1952) was not directly observed, but is the result of a calculation based on the observed radius of the nebula and Strömgren-sphere theory.

These two values can be reconciled only if the interstellar Na/H abundance ratio is at least 10, and possibly as much as 50 times higher than the solar system value. Rather than postulate such a major anomaly, we regard the assumption of formation of the lines in a H II region as at fault.

4. MEZGER and HÖGLUND (1967) have measured the r.m.s. turbulent velocities in a number of H II regions from the profile of the 109 α recombination line of H I. Their values represent averages over a 6′ half-power beam width, and thus contain the effects of both expansion and internal motion. The values of $(\langle v_t^2 \rangle)^{1/2}$ given by MEZGER and HÖGLUND have already had their thermal components removed. After multiplication by $(2/3)^{1/2}$ to render them comparable with b's obtained from the present curve of growth analysis, the b_t values for individual H II regions are found to range from 5.9 to 27.5 km/sec, with a mean of 15.7 km/sec. On the other hand, the b's for Na I, Ca II, and CH^+ in the —15 km/sec cloud at ζ Oph are 2.4, 1.5, and 0.85 km/sec respectively, even without removal of their thermal components. This order-of-magnitude difference in b_t's strongly indicates that the optical lines in ζ Oph are not formed in an H II region.

5. Corroborative evidence of the same kind is provided by the H α radial velocities measured by COURTES, CRUVELLIER and GEORGELIN (1966) at 12 points in the H II region around ζ Oph; I am indebted to Dr. COURTES for providing me with details of this work. The mean velocity is —8 km/sec, with a dispersion of the individual values which corresponds to $b_t = 7$ km/sec. We make no point of the fact that the mean velocity does not agree with either of the strong components of Na I or Ca II; this could be due to systematic motions within the H II region, but as before, the value of the velocity dispersion is clearly characteristic of H II regions and much larger than the curve of growth results.

For the foregoing reasons, we proceed on the H I region assumption, although the contribution of material in the H II region surrounding the star will be taken into account.

Since ζ Oph lies very near or within the material of the Sco-Oph clouds, the contribution of the star must be added to the general galactic radiation field in calculations of the interstellar ionization equilibrium in that neighborhood. The recent line-blanketed B0 V model atmosphere calculated by HICKOK and MORTON (1968) has been chosen to represent ζ Oph; I am indebted to Dr. MORTON for supplying me with this material in advance of publication. The radiation field of ζ Oph as a function of distance from the star was computed from the HICKOK-MORTON πF_ν's and an assumed stellar radius of 8 $\odot$; extinction by intervening interstellar material was not taken into account. The general galactic field tabulated by ZIMMERMANN (1964) for a point 75 pc above the galactic plane was adopted. If u_λ, the radiation density (in ergs cm^{-3} Å^{-1}) at λ is the sum of these two contributions, then the probability of photoionization of a ground-state atom is (sec^{-1})

$$\Gamma = 10^{-8} h^{-1} \int_0^{\lambda_0} a_\lambda \lambda_A u_\lambda d\lambda_A , \tag{8}$$

where the wavelengths are in angstroms, λ_0 is the photoionization threshold of the atom in question and a_λ is the photoionization cross-section (cm^2 atom^{-1}).

The number of recombinations cm^{-3} sec^{-1} of ions and electrons into all bound states of the neutral atom is given by (SEATON, 1951) the radiative recombination coefficient

$$\alpha = A \frac{T_e^{-3/2}}{g_i^{(0)}} \sum_j g_O^{(j)} \exp(I^{(j)}/kT_e) \int_{I^{(j)}}^{\infty} a_\nu^{(j)} (h\nu)^2 \exp(-h\nu/kT_e)\, d(h\nu) , \tag{9}$$

where the summation is over all j bound states of the neutral atom, each with its ionization energy $I^{(j)}$, the g's are the statistical weights (subscripts o and i denote neutral and ion, respectively), and

$$A = \left(\frac{2}{\pi}\right)^{1/2} \frac{1}{(mk)^{3/2} c^2} = 1.991 \times 10^{43}. \tag{10}$$

The α's tabulated by SEATON were used for all elements except Li and Be (see Sec. 5 and note to Table 5). In all cases Γ has been computed anew not only for the special radiation field that is necessary here, but with modern data on the photoionization cross-sections, as follows.

NaI. The laboratory cross-sections of HUDSON and CARTER (1967a) were used from the threshold at $\lambda_0 = 2412$ to 600 Å. Since the radiation field of ζ Oph essentially goes to zero below the HeI limit at 504 Å, and the galactic field vanishes below 912 Å, the small extrapolation below 600 Å is acceptable. The ionization threshold of NaII is at $\lambda_0 = 263$; it is assumed that the production of NaIII is negligible except perhaps in the vicinity of a very hot star.

CaI. From $\lambda_0 = 2028$ to 1660 Å, the recommendations of HUDSON and CARTER (1967b) have been followed: the cross-sections of NEWSOM (1966) have been adopted after multiplication by 1.5, except at the peaks of the strong $\lambda\lambda$1886, 1765 autoionization lines, where HUDSON and CARTER's own values were accepted. Shortward of 1660 Å and as far as 1080 Å, 1.5 times the cross-sections of DITCHBURN and HUDSON (1960) have been used, while below 1080 Å a constant value of $a_\lambda = 1.0$ Mb was assumed[6]. Although full account of the effects of autoionization on Γ are thus taken into account, no allowance for an increase in α due to the inverse process of dielectronic recombination was made.

[6] The value of Γ computed by WEIGERT (1955) for CaI was based on early laboratory cross-sections which were reasonably correct as far as they went, but the data stopped at 1950 Å and thus included only the toe of the a_λ vs. λ curve, which passes through a minimum near 1950 Å and then rises again and attains much higher values.

Table 5. *The photoionization coefficient Γ as it depends on X, the distance from ζ Oph*[a]

X (pc)	HI		HII		HI		HII	
	LiI				BeI			
2	0.294	(—7)	0.297	(—7)	0.292	(—7)	0.293	(—7)
4	.766	(—8)	.774	(—8)	.747	(—8)	.749	(—8)
6	.364	(—8)	.367	(—8)	.345	(—8)	.345	(—8)
10	.158	(—8)	.159	(—8)	.139	(—8)	.139	(—8)
20	.707	(—9)	.710	(—9)	.518	(—9)	.518	(—9)
50	·464	(—9)	.464	(—9)	.274	(—9)	.274	(—9)
90	.432	(—9)	.432	(—9)	.242	(—9)	.242	(—9)
150	.423	(—9)	.423	(—9)	.233	(—9)	.233	(—9)
α	0.61	(—11)	0.19	(—12)	0.63	(—11)	0.20	(—12)
	NaI				KI			
2	0.189	(—8)	0.194	(—8)	0.533	(—8)	0.546	(—8)
4	.489	(—9)	.501	(—9)	.138	(—8)	.141	(—8)
6	.230	(—9)	.235	(—9)	.649	(—9)	.665	(—9)
10	.974	(—10)	.994	(—10)	.275	(—9)	.281	(—9)
20	.415	(—10)	.420	(—10)	.117	(—9)	.119	(—9)
50	.258	(—10)	.259	(—10)	.732	(—10)	.735	(—10)
90	.237	(—10)	.238	(—10)	.674	(—10)	.675	(—10)
150	.232	(—10)	.232	(—10)	.657	(—10)	.658	(—10)
α	0.59	(—11)	0.17	(—12)	0.56	(—11)	0.16	(—12)
	CaI				Ca II			
2	0.185	(—7)	0.187	(—7)	0.287	(—9)	0.324	(—9)
4	.480	(—8)	.488	(—8)	.741	(—10)	.837	(—10)
6	.228	(—8)	.231	(—8)	.347	(—10)	.392	(—10)
10	.984	(—9)	.995	(—9)	.145	(—10)	.165	(—10)
20	.438	(—9)	.441	(—9)	.602	(—11)	.690	(—11)
50	.285	(—9)	.285	(—9)	.364	(—11)	.421	(—11)
90	.265	(—9)	.265	(—9)	.332	(—11)	.386	(—11)
150	.259	(—9)	.259	(—9)	.323	(—11)	.376	(—11)
α	0.60	(—11)	0.17	(—12)	0.35	(—10)	0.17	(—11)

[a] X is the distance of the HI layer iii from the star. The values of α (unit: cm^3 sec^{-1}) are those given by SEATON (1951) for HI ($T_e = 10^2$ °K) and HII ($T_e = 10^4$ °K) conditions, except for LiI and BeI. The contributions to α from captures into the ground states of LiI and BeI were computed from eq. (9) with aid of the laboratory photoionization cross-sections of LiI by HUDSON and CARTER (1967a) and the theoretical cross-sections for BeI by BATES (1946). In both cases, captures into excited states were calculated by the hydrogenic theory of SEATON (1959).

CaII. The theoretical a_λ's of BURGESS and SEATON (1960) were adopted; the threshold is at $\lambda_0 = 1049$ Å.

LiI. The laboratory cross-sections of HUDSON and CARTER (1967a) were used from $\lambda_0 = 2300$ to 575 Å; they were extrapolated linearly to 504 Å. For LiII $\lambda_0 = 165$, so no allowance was made for second ionization.

KI. Laboratory cross-sections by HUDSON and CARTER (1965), reduced with JANAF vapor pressure data, were employed from $\lambda_0 = 2856$ to 1100. From that point to 504 Å, a constant value of $a_\lambda = 0.39$ Mb was assumed. Cross-sections for KI determined by MARR and CREEK (1966) agree approximately with the HUDSON and CARTER results at longer wavelengths, but are lower by a factor of nearly 2 at 1200 Å. No account was taken of second ionization for K, for which $\lambda_0 = 391$.

Values of Γ for these ions are given in Table 5 for a representative range of distances from ζ Oph. They are excerpted from a denser tabulation of values that were used in the actual calculations. The values of Γ in the "HI region" columns represent an integration of eq. (8) from λ_0 to 912 Å. The "HII region" values are based on an integration from λ_0 to 0, or in effect from λ_0 to 504 Å. Values of α are given at the foot of each column. With this information, the concentration n_0 of an atom and n_1 of its ion, at the point specified by the radiation field, can be obtained from

$$\frac{n_1 n_e}{n_0} = \frac{\Gamma}{\alpha} . \tag{11}$$

A model for the stratification of the interstellar material lying between ζ Oph and the sun has to be constructed in order to make proper use of these data. As will be shown, the main contribution to the lines of the —15 km/sec spectrum that are accessible from the earth's surface comes from a thin, dense HI layer, but the following composite model is intended to represent the spectrum more precisely. (i) The HII region of 15 pc radius that appears on direct photographs is assumed to extend an equal distance along the line of sight, with $n(\mathrm{H}) = n_e = 3$ cm^{-3}. The corresponding $\mathfrak{E}$ across a diameter of the region is 270. This value is compatible with the 400 Mc/s continuum observations; a more refined fit to the radio data seems unwarranted. Outside this is (ii), an HI region of the same density $n(\mathrm{H}) = 3$ cm^{-3}, extending only as far as (iii), a very dense, thin HI layer wherein the major part of the line absorption takes place, and whose properties will be determined from the observations. Outside this thin layer is (iv), an HI region of $n(\mathrm{H}) = 0.1$ cm^{-3} extending the remaining distance to the sun. The total length of this line of sight is taken as 170 pc. The density assumed for this last layer of the model is an upper limit for the "intercloud region" near the sun, judging from the results of STRÖMGREN (1948: $n(\mathrm{H}) < 0.1$ cm^{-3}) and of MORTON (1967: $n(\mathrm{H}) = 0.1$ cm^{-3}), but this volume contributes so little to the interstellar lines in the optical region that there is no reason to refine the assumption.

The calculation of the cumulative N's for this model can be illustrated by the case of Ca. Let $R(\mathrm{Ca})$ represent the value of $n(\mathrm{Ca})/n(\mathrm{H})$, and h_1 and h_2 the respective values of Γ/α for CaI and CaII at a particular distance from the star. It is assumed that

$$N(\mathrm{Ca}) = \int [n(\mathrm{Ca\,I}) + n(\mathrm{Ca\,II}) + n(\mathrm{Ca\,III})]\, dr , \tag{12}$$

where r is the radial coordinate, and the integral extends from zero at the star out to the point where N is observed; $r = 170$ pc at the sun. The three integrals in eq. (12) are

$$N(\mathrm{Ca\,I}) = R(\mathrm{Ca}) \int n^3(\mathrm{H}) \frac{\varepsilon^2}{D} dr\,, \tag{13a}$$

$$N(\mathrm{Ca\,II}) = R(\mathrm{Ca}) \int n^2(\mathrm{H}) \frac{\varepsilon h_1}{D} dr\,, \tag{13b}$$

$$N(\mathrm{Ca\,III}) = R(\mathrm{Ca}) \int n(\mathrm{H}) \frac{h_1 h_2}{D} dr\,, \tag{13c}$$

where

$$D = \varepsilon^2 n^2(\mathrm{H}) + h_1 \varepsilon\, n(\mathrm{H}) + h_1 h_2 \tag{13d}$$

and ε is the number of free electrons per H atom. In an H I region, the conventional assumption is that the electrons come predominantly from the photoionization of C, Mg, Si and Fe, whose solar-system abundances lead to $\varepsilon = 6 \times 10^{-4}$. In an H II region, $\varepsilon = 1$. The solar-system values of R for various elements have been taken from a recent compilation by Cameron (1967). With these parameters and the values of h_1, h_2 in Table 5, the integrations of eqs. (13) can be carried out and the contribution of each layer of the model to the N's observed at the sun calculated.

It is obvious from these calculations (the results are given in Table 6) that the interstellar lines formed by regions i, ii and iv together would be very much weaker than the lines actually observed (except for Ca I and Ca II). The burden of fitting the observations must therefore be on layer iii, and as already argued, this must be an H I region. To adjust the model to the observations it is necessary to decide whether the fit is to be made to H and Ca, or to H and Na. It is well known that the interstellar Ca/Na abundance ratio as obtained by correction of the observed N(Ca II)/N(Na I) for differential ionization is much smaller than the solar-system R(Ca)/R(Na). Howard, Wentzel and McGee (1963) have shown that when N(H I) is also available (in their case, from 21-cm observations) and the interstellar R's can therefore be obtained separately, it is the interstellar Ca which is underabundant while Na is approximately normal. Discussion of the ζ Oph data by the same procedure, using the new ionization corrections derived here, leads to the same conclusion. However, the conclusion depends entirely upon the value assumed in the calculation for the H concentration n(H). If in the case of ζ Oph for example, one selected $n(\mathrm{H}) \approx 0.1\ \mathrm{cm}^{-3}$ then the solar-system R(Ca) would fit the Ca II observation, while to represent the observed N(Na I) with the solar-system R(Na), it would be necessary to assume $n(\mathrm{H}) \approx 500\ \mathrm{cm}^{-3}$. Here, we prefer to leave the value of n(H) open and to proceed on the hypothesis that the solar-system R is correct for interstellar Na but not for Ca. The reasons for this decision are as follows. First, the data in Table 6 show that if the solar-system R(Ca) were applicable to the material of the HII region around ζ Oph, then a value of N(CaII) $= 6.4 \times 10^{13}$ cm^{-2} would result from that volume alone. But the observations give N(CaII) $= 5.4 \times 10^{11}$ for the entire line of sight. Therefore a depletion of CaII in the HII region is required by at least a factor 100 if the solar system R(Ca) is to be adopted for the HI layer iii where the CaII lines are actually believed to originate. It is more reasonable to regard the Ca abundance with suspicion wherever the Ca is found. Second, the model constructed on the assumption that the Na abundance is normal can be used to predict N(KI) from the solar-system R(K). The result is in good agreement with observation (Table 6). Thus if the Ca abundance were normal, both Na and K would have to be overabundant by the same very large factor. Third, if Ca were normal then the consequent low value of n(H) would mean that the interstellar CaII lines produced by layer iii would have to originate along the entire line of sight, not in a localized layer of gas near ζ Oph. On the other hand, the heavy dust obscuration in this direction occupies a limited fraction of the far end of the line of sight, near the stars of the Sco-Oph association. Thus there would be implied a major concentration of dust with no corresponding concentration of gas. Although this may not be impossible, it would be surprising in the context of present ideas on the origin of interstellar particles.

For these reasons, Ca is set aside and we investigate the detailed consequences of the hypothesis that n(Na)/n(H) in interstellar space has the same value as in the solar system. In the dense layer iii in front of ζ Oph, the total amount of Na cm^{-3} is

$$n(\mathrm{Na}) = n(\mathrm{Na\,I}) + n(\mathrm{Na\,II}) = n(\mathrm{Na\,I})\left[1 + \frac{h_1}{n_e}\right], \tag{14}$$

where h_1 is the appropriate value of Γ/α for NaI. If t is the thickness of the layer in which the line absorption takes place,

$$n(\mathrm{Na})\, n_e = \frac{N'(\mathrm{Na\,I})}{t}\,[n_e + h_1]\,, \tag{15}$$

where N' represents the value of N after the contributions of regions i, ii and iv have been removed. With n(Na) $= R$(Na) n(H) and $n_e = \varepsilon\, n$(H), then

$$n^2(\mathrm{H}) = \frac{N'(\mathrm{Na\,I})}{R(\mathrm{Na})\,t}\left[n(\mathrm{H}) + \frac{h_1}{\varepsilon}\right]. \tag{16}$$

The values of n(H) and t cannot be separated in eq. (16), and ordinarily some assumption is made about t or its equivalent, n(H). Conventionally, a value of $t \approx 10$ pc is taken. In this case the question can be resolved without making this assumption. Dr. T. E. STECHER has very kindly informed me of his recent observation of the interstellar Lα absorption line in ζ Oph. His measured equivalent width of 15 Å leads to N(HI) $= 4.2 \times 10^{20}$ cm^{-2}. If this value is corrected to N'(HI) by removing the

Table 6. *Predicted number of ions cm⁻² out to the boundaries of the various layers in the composite model, for three assumptions as to the position of the dense HI layer*

From r = [pc]	to r =	Ionization	n (H) [cm⁻³]	N (LiI)	N (LiII)	N (BeI)	N (BeII)	N (NaI)	N (NaII)
If dense HI layer at 15 pc:									
0.0	15.0	HII	3.	0.06 (+9)	2.40 (+11)	1.12 (+6)	3.68 (+9)	0.19 (+13)	0.34 (+15)
15.0	15.136	HI	880.	2.24 (+9)	8.76 (+11)	4.47 (+7)	1.34 (+10)	4.90 (+13)	1.19 (+15)
15.136	170.	HI	0.1	2.24 (+9)	9.59 (+11)	4.47 (+7)	1.47 (+10)	4.90 (+13)	1.31 (+15)
If dense HI layer at 20 pc:									
0.0	15.0	HII	3.	0.06 (+9)	2.40 (+11)	1.12 (+6)	3.68 (+9)	0.19 (+13)	0.34 (+15)
15.0	20.0	HI	3.	0.06 (+9)	3.20 (+11)	1.14 (+6)	4.91 (+9)	0.19 (+13)	0.45 (+15)
20.0	20.146	HI	730.	2.20 (+9)	8.88 (+11)	4.74 (+7)	1.36 (+10)	4.89 (+13)	1.21 (+15)
20.146	170.	HI	0.1	2.20 (+9)	9.68 (+11)	4.74 (+7)	1.48 (+10)	4.89 (+13)	1.32 (+15)
If dense HI layer at 50 pc:									
0.0	15.0	HII	3.	0.06 (+9)	2.40 (+11)	1.12 (+6)	3.68 (+9)	0.19 (+13)	0.34 (+15)
15.0	50.0	HI	3.	0.17 (+9)	8.00 (+11)	1.40 (+6)	1.23 (+10)	0.22 (+13)	1.13 (+15)
50.0	50.168	HI	540.	2.21 (+9)	1.28 (+12)	5.58 (+7)	1.96 (+10)	4.90 (+13)	1.76 (+15)
50.168	170.	HI	0.1	2.21 (+9)	1.34 (+12)	5.58 (+7)	2.06 (+10)	4.90 (+13)	1.85 (+15)
Observed N =				<1.9(+10)	—	—	<8.3(+10)	4.9 (+13)	—

From r = [pc]	to r =	Ionization	n (H) [cm⁻³]	N (CaI)	N (CaII)	N (CaIII)	N (KI)	N (KII)
If dense HI layer at 15 pc:								
0.0	15.0	HII	3.	0.04 (+12)	0.64 (+14)	3.29 (+14)	0.21 (+11)	1.74 (+13)
15.0	15.136	HI	880.	3.93 (+12)	7.82 (+14)	6.53 (+14)	8.61 (+11)	6.27 (+13)
15.136	170.	HI	0.1	3.93 (+12)	7.82 (+14)	7.88 (+14)	8.61 (+11)	6.87 (+13)
If dense HI layer at 20 pc:								
0.0	15.0	HII	3.	0.04 (+12)	0.64 (+14)	3.29 (+14)	0.21 (+11)	1.74 (+13)
15.0	20.0	HI	3.	0.40 (+12)	0.65 (+14)	4.59 (+14)	0.21 (+11)	2.32 (+13)
20.0	20.146	HI	730.	4.05 (+12)	7.33 (+14)	7.21 (+14)	8.67 (+11)	6.36 (+13)
20.146	170.	HI	0.1	4.05 (+12)	7.33 (+14)	8.52 (+14)	8.67 (+11)	6.94 (+13)
If dense HI layer at 50 pc:								
0.0	15.0	HII	3.	0.04 (+12)	0.64 (+14)	3.29 (+14)	0.21 (+11)	1.74 (+13)
15.0	50.0	HI	3.	0.04 (+12)	0.77 (+14)	1.23 (+15)	0.26 (+11)	5.79 (+13)
50.0	50.168	HI	540.	4.08 (+12)	6.71 (+14)	1.42 (+15)	8.64 (+11)	9.20 (+13)
50.168	170.	HI	0.1	4.08 (+12)	6.71 (+14)	1.52 (+15)	8.64 (+11)	9.66 (+13)
Observed N =				<1.3(+10)	5.4 (+11)	—	8.0 (+11)	—

contributions of foreground and background gas in the line of sight[7], then t in eq. (16) can be identified with $N'(\mathrm{HI})/n(\mathrm{H})$, and so

$$n(\mathrm{H}) = \frac{C}{1-C}\,\frac{h_1}{\varepsilon} \qquad (17\,\mathrm{a})$$

where

$$C = \frac{N'(\mathrm{Na\,I})}{R(\mathrm{Na})\,N'(\mathrm{HI})}\,. \qquad (17\,\mathrm{b})$$

Depending somewhat upon the distance from the star where this layer iii is located, the result is that $n(\mathrm{H}) = 500$ to $900\ \mathrm{cm}^{-3}$ and the thickness of the layer $t = 0.15$ pc. A similar result is obtained from the KI abundance.

This procedure can in principle be used to determine $n(\mathrm{H})$ and t from the observed N's of any two elements, provided their abundances with respect to H are known. If it is based on two minor constituents however, the result is highly sensitive to small errors in the abundances. The present example is very favorable because one element is H, but if $N(\mathrm{HI})$ were erroneously assumed to be $y \cdot N(\mathrm{HI})$, then the result would be $n(\mathrm{H})/y$. Since in this case the interstellar Lα line is saturated, $N(\mathrm{HI})$ is proportional to the square of its equivalent width, and so the values of $n(\mathrm{H})$ derived here are subject to considerable uncertainty through the observational error in measuring $W^{(\lambda)}$.

The unconventionally high values of $n(\mathrm{H})$ obtained in this way could be reduced by a proportional increase in the value of ε. The possibility that the level of ionization in HI regions might be raised significantly by low-energy cosmic-ray particles has been suggested by HABING and POTTASCH (1967). It may be possible to determine n_e in the dense HI layer in front of ζ Oph, but unfortunately this will not test the HABING and POTTASCH proposal unless $n(\mathrm{H})$ can be determined independently.

With the lines accessible from the earth's surface, the most promising means of determining n_e is through the observed value of $N'(\mathrm{Ca\,I})/N'(\mathrm{Ca\,II})$ provided that the abnormally low Ca abundance as inferred from CaI and CaII is not due to an anomalously high degree of ionization. With this proviso,

$$n_e = \frac{N'(\mathrm{Ca\,I})}{N'(\mathrm{Ca\,II})}\,h_1(\mathrm{Ca\,I})\,. \qquad (18)$$

The correction of the observed N to N' was made by assuming that the Ca abundance deficiency is the same everywhere along the line of sight, so that at a distance of 20 pc from ζ Oph where $h_1(\mathrm{Ca\,I}) = 73$ (Table 5), the value of $N'(\mathrm{Ca\,I})/N'(\mathrm{Ca\,II}) < 0.026$, and therefore $n_e < 1.9\ \mathrm{cm}^{-3}$. On the other hand, at this distance from the star the expected value is $n_e = \varepsilon\, n(\mathrm{H}) = 0.4\ \mathrm{cm}^{-3}$. The observational upper limit on n_e is set by the fact that

[7] All this HI is attributed to the —15 km/sec cloud, because no component of the 21-cm line at a displacement of —29 km/sec is apparent on the Green Bank scans.

Ca I λ4227 is not detectable on the present spectrograms of ζ Oph, and thus $W^{(\lambda)} < 3$ mÅ. A relatively moderate improvement in the instrumental threshold might make possible the positive detection of the λ4227 line.

Table 6 contains the results of calculations based on eqs. (13) for the ions of interest, out to the boundaries of the various layers in the model and finally, at the sun. Three alternative assumptions were made as to the location of the dense H I layer iii: at 15, 20 or 50 pc from the star. If this layer is located near the star at the edge of the H II region, then it has to be somewhat denser (n(H) $= 880$ cm^{-3}) than if it is 50 pc away (n(H) $= 540$ cm^{-3}). The thickness is nearly the same in all cases: about 0.15 pc. The layer cannot be very much farther from ζ Oph than 50 pc, because then — if it is assumed that the dark material is also concentrated in this dense region — there would be increasing conflict with the result from star counts that the obscuration in this direction is 100 pc or more from the sun (Bok, 1956). It does not seem possible to decide from the present observations where in the interval 15 to 50 pc from the star this dense layer actually lies.

When the model is thus fitted to the H I and Na I data, the abundance of K I that is predicted lies quite close to the observed value. (The observed N's are collected at the bottoms of the columns of Table 6 for comparison with prediction.) However, Ca as represented by both Ca I and Ca II is grossly deficient with respect to the solar system: from the absence of Ca I λ4227 by a factor > 300, and from the Ca II lines by about a factor 1400. It must be emphasized that the very large Ca I, Ca II underabundance in ζ Oph is numerically not representative because the Ca II lines in ζ Oph are unusually weak. Seaton pointed out (1951) that in a sample of 14 distant stars for which data on both Ca II und Na I were available, the average value of N(Ca II)/N(Na I) is about unity. Yet in the —15 km/sec spectrum of ζ Oph it is about 0.01[8]. The underabundance of Ca I, Ca II is exaggerated in ζ Oph for some reason but it is none the less real and should not be ignored on the grounds that the effect is less extreme elsewhere. The point is rather that even when the most modern data on the radiation field and photoionization cross-sections are used in a relatively simple geometrical situation, all of which should increase the plausibility of the calculations, a major deficiency of Ca still exists provided that the Na/H abundance is normal. It should be mentioned that the mechanism of preferential collisional ionization of Ca II over Na I that was suggested by Routly and Spitzer (1952) to explain the apparent

[8] It would not of course be correct to multiply the Ca I and Ca II deficiencies quoted for ζ Oph by this factor and conclude that in most interstellar spectra, the discrepancy is rather small. The proper radiation fields should be used in correcting the observed N values in each individual case.

deficiency of Ca in high-velocity clouds ought not to be operative in the —15 km/sec cloud at ζ Oph, which is almost stationary in the local standard of rest.

There seems also to be a large deficiency of Ti in the —15 km/sec spectrum, but here the photoionization corrections are unknown and a rougher argument must be made. The ionization potential of Ti II is 13.57 ev, so near the Lyman limit at 13.595 ev that in an H I region all Ti will exist as Ti I or Ti II[9]. Therefore, since the solar-system abundance ratio of Ti/H is 8.8×10^{-8}, STECHER's value for N(H I) indicates that there should be at least 3.7×10^{13} Ti I + Ti II atoms cm^{-2}. Resonance lines of both Ti I and Ti II lie at terrestrially accessible wavelengths but neither can be detected in the —15 km/sec cloud, although Ti II is present in the —29 km/sec spectrum. From Table 3, $N(\mathrm{Ti\,I} + \mathrm{Ti\,II}) < 3 \times 10^{11}\ \mathrm{cm}^{-2}$, indicating a Ti deficiency of more than a factor 100.

The problem of the missing Ca and Ti may be clarified by observations from outside the earth's atmosphere. But in the case of Ca, the question whether there has been a major transfer of Ca I and Ca II to Ca III by some neglected ionization process will not be answered readily because the resonance lines of Ca III lie at 403, 409, 490 Å, in a spectral region where the continuous opacity of the interstellar gas is high. Ti is a better case for such a test because the strongest interstellar lines of Ti III are at 1291, 1295, 1298 Å.

4. The Molecular Abundances

The present analysis of the molecular lines follows the formalism advocated by SCHADEE (1967), whose paper discusses the assumptions and complications involved. For the present purpose, we identify with each interstellar line corresponding to an electronic transition between J', v' and J'', v'' a total oscillator strength

$$f = \frac{\lambda(v', v'')}{\lambda(J', J'')} f_{el}[\lambda(v', v'')]\, q(v', v'')\, \frac{S_J}{2J'' + 1}\,. \tag{19}$$

Here, $\lambda(v', v'')$ and $\lambda(J', J'')$ represent the wavelengths of the band origin and of the rotational line in question, respectively; S_J is the Hönl-London factor normalized according to SCHADEE's convention; $q(v', v'')$ is the Franck-Condon factor; f_{el} is the component of f that is characteristic of the electronic transition. It varies with λ across the band system. As usual, single primes represent the upper state and double primes the lower. The product $f_{el}q$ can be obtained from τ, the radiative lifetime of the upper state n', v', corrected for branching to other low levels where necessary:

$$f_{el}[\lambda(v', v'')]\, q(v', v'') = \frac{mc\lambda^2}{8\pi^2 e^2} \frac{d(n', v')}{d(n'', v'')} [\tau(n', v')]^{-1}. \tag{20}$$

[9] Even in an H II region, the magnitude of the Lyman jump in all but the hottest stars is such as to hamper severely the production of Ti III.

Here, the d's are degeneracy factors to take account of unresolved Λ-type and spin doubling; $d = (2S + 1)$ for Σ states and $2(2S + 1)$ for all others. The λ is a properly weighted mean wavelength. Once the value of f is obtained for a molecular line, the procedure follows that described for the atomic case. The analysis of each molecule is described here in sufficient detail that adjustments may readily be made as new data on the f-values become available.

CH^+

The $A^1\Pi - X^1\Sigma^+$ system of CH^+ has been analyzed by Douglas and Herzberg (1942) and by Douglas and Morton (1960). The $R(0)$ lines of the 0—0, 1—0, 2—0 and 3—0 bands are observed in ζ Oph, and that of 4—0 is suspected as well (see Table 1, Note 14). No measurement of the absolute f-value of CH^+ has been reported; in view of the astronomical importance of this spectrum, such an experiment is strongly recommended. It is possible to derive some information from the Franck-Condon factors alone, however. Dr. R. W. Nicholls has at my request very kindly calculated q's for this band system on the Morse approximation to the potential curve, and with Douglas and Morton's constants; they are given in Table 7 for the bands of interest here. On the assumption that f_{el} is independent of λ, a plot of $\log W^{(\lambda)}/\lambda$ against $\log q(v', v'') \cdot \lambda(v', v'')$ for the CH^+ lines can be adjusted for best fit to the theoretical curve of growth. From the fit of the three stronger CH^+ lines, one obtains $Nf_{el} = 5.7 \times 10^{11}$ cm^{-2}, $b = 0.85$ km/sec. A somewhat better approximation may be that the quantity $\Sigma R_e^2(r)$, involved in f_{el}, does not change sensibly with internuclear distance r (Schadee, 1967). If so, then f_{el} varies as λ^{-1}. In such a case, $W^{(\lambda)}/\lambda$ would be proportional to q, not to $q\lambda$, but trial shows that this difference in abscissae does not affect the fit over the wavelength range considered here (3745—4232 Å) on account of the scatter in the measured $W^{(\lambda)}$'s. We therefore accept the above values, which will yield $N(CH^+)$ once a value of f_{el} has been measured.

CH

Three electronic systems of CH occur in the accessible region of the spectrum, and all the expected interstellar lines from $X^2\Pi$, $v'' = 0$, $J'' = 1/2$ have now been observed. On the assumption that the value of $b = 0.85$ km/sec from CH^+ applies to CH as well, the N(CH) values for the $A^2\Delta - X^2\Pi$ and $B^2\Sigma - X^2\Pi$ system lines have been read out of the curve of growth by use of the $q(0,0)\, f_{el}$ values derived from lifetime measurements by Fink and Welge (1967). The results from individual lines are given in Table 8. No measured f-value has apparently been published for the $C^2\Sigma - X^2\Pi$ system. Since for all three systems the N(CH) value refers to the same rotational level, an estimate of $f(C - X)$

can be made as follows. The four lines of the $A - X$ and $B - X$ systems give a mean $N(\mathrm{CH}) = 4.3 \times 10^{13}$, wherein $\lambda 3878$ was assigned only half weight. From the three $C - X$ lines, the mean $N(\mathrm{CH})/q(0, 0)\, f_{el}$

Table 7. *Franck-Condon Factors for CH^+ [$A^1\Pi - X^1\Sigma$], computed by* R. W. Nicholls

v', v''	$q\,(v', v'')$
0,0	0.538
1,0	0.287
2,0	0.106
3,0	0.037
4,0	0.014
5,0	0.0057

Table 8. *Interstellar lines of CH in ζ Oph*

λ	Line	$q\,(0, 0)\, f_{el}$	$\frac{S_J}{2J''+1}$	Nf	N
$A^2\Delta - X^2\Pi$, 0—0 band:					
4300	$R_2\,(1)$	5.2 (—3)	1.00	1.99 (+11)	3.8 (+13)
$B^2\Sigma - X^2\Pi$, 0—0 band:					
3890	${}^PQ_{12}\,(1)$	2.8 (—3)	0.333	4.67 (+10)	5.0 (+13)
3886	$Q_2\,(1) + {}^QR_{12}\,(1)$	2.8 (—3)	0.500	4.98 (+10)	3.7 (+13)
3878	$R_2\,(1)$	2.8 (—3)	0.167	2.4: (+10)	5.0: (+13)
$C^2\Sigma^+ - X^2\Pi$, 0—0 band:					
3146	${}^PQ_{12}\,(1)$	—	0.333	6.45 (+10) [a]	—
3143	$Q_2\,(1) + {}^QR_{12}\,(1)$	—	0.500	1.01 (+11) [a]	—
3137	$R_2\,(1)$	—	0.167	5.03 (+10) [a]	—

[a] These are $Nq\,(0, 0)\, f_{el}$.

Table 9. *Interstellar lines of CN* [$B^2\Sigma^+ - X^2\Sigma^+$, 0—0] *in ζ Oph*

λ	Classification	$q\,(0, 0)\, f_{el} \frac{\Sigma S_J}{\Sigma(2J''+1)}$ [a]	$N\,(N'')$ [b]
3874.61	$R_1\,(0) + {}^RQ_{21}\,(0)$	1.73 (—2)	4.8 (+12)
3874.00	$R_1\,(1) + R_2\,(1) + {}^RQ_{21}\,(1)$	6.9 (—3)	3.9 (+12)
3875.76	$P_1\,(1) + {}^PQ_{12}\,(1)$	5.8 (—3)	≦2.6: (+12)

[a] The absolute f-value of 1.9 (—3) for the 0—0 band, determined by Reis (1965), was used. Halmann and Laulicht (1966) give $q\,(0, 0) = 0.909$. The rotation term is explained in the text.

[b] N'' is the lower rotational quantum number, specifying angular momentum without spin.

$= 7.2 \times 10^{10}$, whence $f_{el}(C-X) = 1.7 \times 10^{-3}$, since $q(0, 0) = 1.00$ according to HALMANN and LAULICHT (1966). Possibly this is the first estimate of a molecular f-value from observations of interstellar lines.

From the relative f-values, one expects that the $Q_2(1) + {}^QR_{12}(1)$ line of the 1—0 band, $B-X$ system of CH at 3633.29 Å might be detectable. It should have an equivalent width 0.19 that of the same line in the 0—0 band, or about 1 mÅ. There seems to be an exceedingly faint, sharp line very near this position on the best 1.3 and 2.0 Å/mm plates of ζ Oph, but it is too marginal a feature to be certain of its reality.

No account has been taken here of the fact that the ground rotational level of CH is Λ-doubled with a splitting of 0.101 cm^{-1} according to GOSS (1966). The N(CH)'s quoted refer to the sum of the populations of both levels, since this is the convention contained in SCHADEE's f-values.

CN

Three rotational lines of the λ3883 CN band are observed in interstellar absorption in ζ Oph. They originate in the $N'' = 0$ and 1 levels, which have an energy difference of 3.94 cm^{-1}. Because of the further spin doubling of three of the four levels involved ($N'' = 0$ is single), each rotational line is either an unresolved doublet or triplet, and allowance must be made for this in obtaining the populations. If the population of each spin-doubled level with the same N'' is in proportion to its statistical weight $2J'' + 1$, then the total $N(N'')$ will be obtained if in eq. (19) one uses instead of $S_J/2J'' + 1$ the corresponding sum over all the unresolved lines: $\Sigma S_J/\Sigma(2J'' + 1)$. For $N'' = 0$, this becomes $\Sigma S_J/2J'' + 1$. Other details and the results are given in Table 9. The total N (for $N'' = 0 + N'' = 1$) is $N(\mathrm{CN}) = 8.7 \times 10^{12}$ cm^{-2}. The ratio of populations corresponds to a rotational temperature of 3°.1. A similar result was obtained by FIELD and HITCHCOCK (1966) from the same data, namely 3°.3 without allowance for saturation but 2°.8 under a rather extreme allowance for departure from eq. (5).

The corresponding lines of the 1—0 CN band near 3590 Å should be weaker than those of 0—0 by the factor $\lambda^2(1,0)\, q(1,0)/\lambda^2(0,0)\, q(0,0) = 0.085$, so that the $R(0)$ line at 3580 Å should have $W^{(\lambda)} \approx 0.8$ mÅ. A line of that strength might be detectable at 1.3 Å/mm by special effort, but it cannot be seen with assurance on conventional 1.3 and 2.0 Å/mm plates of the region. No lines of the red system of CN$(A^2\Pi_i - X^2\Sigma^+)$ have been detected in interstellar absorption, but the system is handicapped by a small f-value (JEUNEHOMME, 1965). Probably the most favorable line for photographic detection would be $R_1(0)$ of the 2—0 band at 7906.60 Å, but the vicinity is confused by atmospheric H_2O lines.

OH

Four lines of the 0—0 band, $A^2\Sigma - X^2\Pi_i$ system of OH occur near 3080 Å. Two of these lines are close doublets that are not expected to be resolved with the present spectroscopic resolution. The lines are listed in Table 10, which gives other details. No distinction is made here between lines originating from different Λ-components of the ground state, since the splitting is only 0.055 cm^{-1}. Three 2.0 Å/mm spectrograms of ζ Oph are well exposed in this region, but no lines are present near 3078 or 3081 Å, where the two stronger OH features should occur. The corre-

Table 10. *Rotational lines of OH* [$A^2\Sigma - X^2\Pi_i$, 0—0] *expected in interstellar absorption*

λ	Classification[a]	f[b]
3078.44, .47	$Q_1\left(\frac{3}{2}\right) + Q_{21}\left(\frac{3}{2}\right)$	3.8 (—4)
3064.40	$S_{21}\left(\frac{3}{2}\right)$	0.20 (—4)
3081.66	$P_1\left(\frac{3}{2}\right)$	2.4 (—4)
3072.06, .01	$R_{21}\left(\frac{3}{2}\right) + R_1\left(\frac{3}{2}\right)$	1.6 (—4)

[a] The branch notation is that used by Dieke and Crosswhite (1962). The more conventional notation is shown by Jevons (1932, p. 164). The first two lines have the c level as lower state, the last two have the d level.

[b] These f's are obtained from $f = q\,(0,0)\, f_{el} S_J/2\,J'' + 1$, where $q(0,0)\, f_{el}$ is taken as 8.0 (—4) and for the blends the total S_J is used. The S_J's are the "rotational transition probabilities" tabulated by Dieke and Crosswhite but divided by 8, to make them conform to Schadee's (1967) sum-rule convention. These f-values are one-half those quoted by Goss and Spinrad (1966).

Table 11. *Rotational lines of NH* [$A^3\Pi_i - X^3\Sigma^-$, 0—0] *expected in interstellar absorption*

λ	Classification	f[a]
3358.06	$R_1\,(0)$	4.3 (—3)
3353.92	$^RQ_{21}\,(0)$	2.5 (—3)
3351.71	$^RP_{31}\,(0)$	0.93 (—3)
3347.32	$^SR_{21}\,(0)$	0.18 (—3)
3345.59	$^SQ_{31}\,(0)$	0.14 (—3)
3335.53	$^TR_{31}\,(0)$	0.02 (—3)

[a] S_J's conforming to Schadee's sum rule were obtained by multiplying Dixon's (1959) "rotational line strengths" by 3. The f-values of the last column are based on these S_J's and the value of $q\,(0,0)\, f_{el} = 8.0$ (—3) measured by Bennett and Dalby (1960b).

sponding upper limit on their $W^{(\lambda)}$'s was estimated in two ways: (i) from the invisibility on the same plates of the Ti II λ3072 line in the —29 km/sec spectrum. This Ti II line should have $W^{(\lambda)} = 1.9$ mÅ, if one scales down the measured equivalent width of Ti II λ3383. (ii) λ3137, the weakest of the three CH lines near that wavelength should have $W^{(\lambda)} = 2.5$ mÅ on the basis of the measured $W^{(\lambda)}$'s of the two stronger CH lines in the same band. CH λ3137 can be seen weakly but distinctly on these spectrograms. Therefore, it is concluded that OH λ3078, the strongest of the four OH lines, must have $W^{(\lambda)} < 2.5$ mÅ, from which $N(\mathrm{OH}) < 8.3 \times 10^{13}$ cm^{-2}.

NH

The 0—0 band of the $A^3\Pi_i - X^3\Sigma^-$ system of NH, near 3360 Å, should under interstellar conditions reduce to the six lines from $N'' = 0$ which are listed in Table 11, based on the analysis of Dixon (1959). No sign of the stronger of these lines can be seen on three 2.0 Å/mm plates of ζ Oph, or on plates of the same dispersion of several other even more heavily reddened stars. Certainly $W^{(\lambda)} < 3$ mÅ in ζ Oph for the strongest NH line to be expected, λ3358. Therefore $N(\mathrm{NH}) < 7.4 \times 10^{12}$ cm^{-2}.

A search was also made for interstellar lines of MgH, SiH and CO^+ since absolute f-values are known for those molecules. None were found. The details are given in Table 12, and the upper limits on the abundances in Table 3.

One may now compare the molecular abundances observed in ζ Oph (Table 3) with the expectations of some theories of molecule formation. In Table 13 are listed the relative abundances of 4 molecules, expressed in units of $N(\mathrm{CH}) + N(\mathrm{CH}^+)$. However, this quantity has been taken as equal to $2N(\mathrm{CH})$ since the f-value of CH^+ is for the moment unknown. In the theory of Stecher and Williams (1966) of molecule formation by exchange reactions on graphite surfaces, the activation energy of the reaction (0.2 to 0.4 ev for these particular molecules) is provided by the kinetic energy of the incident atom. Molecule formation by this means is thus severely handicapped in H I regions, where $\overline{mv^2/2}$ is only about 10^{-2} ev. Therefore, Stecher and Williams consider means of either raising the cloud temperature by a moderate amount, or increasing the energy of the impinging atoms. Specific mechanisms which they investigate to these purposes are cloud-cloud-collisions, or the driving of the grains through the gas by radiation pressure of a hot star. Putting aside the question whether graphite grains exist at all in space, neither of these processes seems applicable to the present situation at ζ Oph[10]. In fairness, therefore,

[10] Speculation as to what the situation may have been in the past are irrelevant because of the very short lifetime of these molecules in the radiation field: about 100 years for CH at 20 pc from the star.

the ζ Oph data should not be used in judging the absolute effectiveness of the STECHER-WILLIAMS mechanism, but the predictions of their theory for the relative yields should measure the validity of the basic idea. Table 13

Table 12. *Details on molecular lines sought, but not found in ζ Oph*

λ	Classification	$\frac{S_J}{2J''+1}$	Number of spectrograms examined	Dispersion (Å/mm)	Upper limit on $W^{(\lambda)}$ (mÅ)	Note
MgH: $A^2\Pi - X^2\Sigma^+$, 0—0:						
5187.06	$Q_1\left(\frac{1}{2}\right)$	0.333	3	4.1	3	a
5183.15	$R_1\left(\frac{1}{2}\right)$	0.410				
5175.45:	${}^SR_{21}\left(\frac{1}{2}\right)$	0.256				
SiH: $A^2\Delta - X^2\Pi$, 0—0:						
4119.48	$R_{21}\left(\frac{1}{2}\right)$	2.0	3	2.0	2	b
CO+: $A^2\Pi_i - X^2\Sigma^+$:						
Band	λ of $R_{21}\left(\frac{1}{2}\right)$	f				
1—0	4542.17	6.4 (—4)	—	—	—	c
2—0	4250.94	5.6 (—4)	2	2.0	3	
3—0	3999.08	5.2 (—4)	2	1.3, 2.0	3	
4—0	3779.18	5.0 (—4)	2	1.3, 2.0	3	

Notes:

[a] MgH: The wavelengths for the first two lines are from GUNTSCH (1939); the last is extrapolated. The S_J's were calculated from SCHADEE's (1964) Case *b* formulae, normalized to his 1967 convention. A value of $q(0, 0)\, f_{el} = 8.0$ (—3) was estimated by SCHADEE (1964) from the strength of the MgH band in the solar spectrum and the calculated amount of MgH above the photosphere. This last involves an assumption as to the value of D_0° for MgH $X^2\Sigma^+$, which is not well known. If SCHADEE's assumption that $D_0^\circ = 2.49$ ev is too high, then q (0, 0) f_{el} must be raised accordingly. But MAIN, CARLSON and DUPUIS (1967) from a laboratory experiment conclude that q (0, 0) $f_{el} \lesssim 2.0$ (—3). The value of N (MgH) in Table 3 is based on SCHADEE's value.

[b] SiH: Only the one line arises from the ground state in bands of this system (DOUGLAS, 1957). From a tentative identification of SiH on the solar disc, SCHADEE (1964) estimated that q (0, 0) $f_{el} = 2.4$ (—3), upon which the abundance in Table 3 is based. A single band of another system of SiH has been classified as ${}^2\Sigma^+ - X^2\Pi$, 0—0, by VERMA (1965). Probably the strongest interstellar line of this band would be R_1 (1/2) + ${}^RQ_{21}$ (1/2) at 3233.60 Å. Two good 2.0 Å/mm spectrograms of ζ Oph show no line as strong as 3 mÅ at this position.

[c] CO+: The f_{el} value is divided between many v'—0 bands, and hence none of the possible interstellar lines are dominant. The wavelengths of R_{21} (1/2), the strongest line, are listed for several bands. The f's are derived from the lifetime measurement of BENNETT and DALBY (1960a).

contains the relative concentrations of CH, NH, OH and CN expected under two assumptions: (i) that equilibrium has been reached after a single cloud-cloud collision, or (ii) the molecules are formed on particles driven through the gas by radiation pressure.

Clearly, case (ii) does not represent the data; NH and OH are underabundant by at least one power of ten with respect to prediction. Case (i) does not conflict so decisively with the observations. Not shown in Table 13 is the fact that in case (i) the abundance of H_2 would be about 10^9 times that of CH. Now, it is observed that in front of ζ Oph the ratio $n(\mathrm{H\,I})/n(\mathrm{CH})$ is about 10^7, so that it would be supposed that the total $n(\mathrm{H} + \mathrm{H}_2)$ concentration must be 10^2 times higher than the $n(\mathrm{H})$ values of 500 to 900 cm^{-3} that were derived earlier. Some supporting evidence would be necessary before one could accept total densities of the order of $10^5\ \mathrm{cm}^{-3}$.

The low abundance of NH and OH with respect to CH does not appear to be due to photoionization. The location of the photoionization thresholds of NH and OH so near the Lyman limit (Table 13) indicates that the probability of this process taking place is low, particularly under H I region conditions. This statement is supported by the fact that neither NH^+ or OH^+ are observed in ζ Oph. Although f-values are not known for these molecular ions, if the oscillator strengths were comparable with those in the isoelectronic molecules CH and NH the ions would be detectable, if this were in fact the explanation for the lack of NH and OH.

One is therefore inclined to regard the low relative abundance of OH and NH as real. It is extremely suggestive that just such a suppression of OH and NH with respect to CH and CN is to be expected if molecules are predominantly formed by 2-body recombination in interstellar space (see the last line of Table 13). This process has not been in favor in recent years, largely as a result of the work of Bates and Spitzer (1951). They studied the gas-phase processes, as distinct from those involving solid surfaces, that are relevant to the formation of CH and CH^+. They considered the equilibrium that is reached in an H I region as the result of competition between recombination and radiative association on the one hand, and photoionization and photodissociation on the other. The best estimates then possible for the various rate coefficients led to the conclusion that agreement between the observed and theoretical concentrations of interstellar CH was achieved only for values of $n(\mathrm{H})$ in the neighborhood of $10^3\ \mathrm{cm}^{-3}$. Bates and Spitzer regarded this density as unacceptable in view of Strömgren's (1948) result that $n(\mathrm{H})$ rarely exceeds 20 cm^{-3} in interstellar H I clouds. Or in other words, at $n(\mathrm{H}) = 20\ \mathrm{cm}^{-3}$ the equilibrium density of CH would be about 10^3 times lower than actually observed. This result seemed so unassailable except in minor detail that it caused attention to be turned toward other, hopefully more

Table 13. *Relative abundances of molecules in the* −15 km/sec *spectrum at* ζ *Oph*

Molecule	$CH+CH^+$	NH	OH	CN
Observed relative abundance	1.0	<0.075	<0.85	0.09
Relative abundance from Stecher-Williams theory				
i) After one cloud-cloud collision	1.0	0.25	1.5	0.1
ii) Near a hot star	1.0	0.8	13.	0.02
Ionization potential of the neutral molecule (Wilkinson, 1958), ev:	10.64	13.10	13.36 (±0.2)	14.2 (±0.3)
Is the ionized molecule detected at ζ Oph?	yes	no[a]	no	no[b]
Can the neutral molecule be formed by 2-body radiative recombination?	yes[c]	no	no[d]	yes

Notes:

[a] The analysis of NH^+ by Colin and Douglas (1968) indicates that interstellar lines from $X^2\Pi$ are to be expected at 4353 Å and near 4630 Å. No such lines are found in ζ Oph.

[b] If the ground state of CN^+ is the $a^1\Sigma$ state of Douglas and Routly (1954): see Herzberg (1955).

[c] Only if the collisions are non-adiabatic (Bates and Spitzer, 1951; Herzberg, 1955).

[d] Herzberg (1955) pointed out that OH could be formed by radiative recombination if the unobserved $^2\Sigma^-$ state were stable. Mulliken (1932) predicted however that $^2\Sigma^-$ was repulsive, and there appears to be no direct evidence to the contrary. Naegeli and Palmer (1967) have interpreted a predissociation in the $A^2\Sigma^+$ levels of OH as due to the effect of a repulsive state that could be either $^2\Sigma^-$ or $^4\Pi$. Inverse predissociation by this route could in principle form OH molecules from ground-state atoms, except that Naegeli and Palmer's results indicate that the collision partners would have to provide kinetic energies of about 0.38 ev to reach the threshold for this process. Such energies would not be available in ordinary H I regions.

efficient processes for molecule production than 2-body radiative recombination.

However the present investigation has shown that densities of the order of those required by the Bates-Spitzer theory are in fact found in at least one interstellar cloud, which also happens to be very abundant in molecules: the dense H I layer in front of ζ Oph[11]. The numerical results of Bates and Spitzer cannot be taken over directly because the radiation field near ζ Oph differs significantly from the one that they considered, so

[11] Of course, densities of this order also are found in dense H II regions. In the central part of the Orion Nebula, n_e becomes as high as 10^4 cm^{-3}. Presumably n(H I) was equally high before that volume became ionized.

Table 14. *Theoretical and observed* CH *and* CH^+ *concentrations in the dense* HI *cloud in front of* ζ *Oph* (*the assumptions involved correspond to* BATES *and* SPITZER's (1951) Case 2.1)

X (pc)	$n\,(CH)_{theor.}$	$n\,(CH)_{obs.}$	$\frac{n(CH)_{obs.}}{n(CH)_{theor.}}$	$n\,(CH^+)_{theor.}$	$\frac{n(CH^+)_{obs.}}{n(CH^+)_{theor.}}$ [a]
15	2.6 (—6)	1.0 (—4)	39.	4.0 (—4)	0.25
20	2.6 (—6)	9.5 (—5)	36.	3.3 (—4)	0.29
50	2.8 (—6)	8.3 (—5)	30.	2.3 (—4)	0.36

[a] No observational value of $n\,(CH^+)$ is available for lack of the f-value. The values in the last column are obtained on the assumption that $n\,(CH^+)_{obs.} = n\,(CH)_{obs.}$.

Table 15. *Triatomic molecules specifically sought in* ζ *Oph, with negative results*

Molecule	λ	Estimated $W^{(\lambda)}$	Analysis
CNC	3294	<3 mÅ	MERER and TRAVIS (1966)
CCN	4698	<5	MERER and TRAVIS (1965)
NCN	3290	<3	HERZBERG and TRAVIS (1964)
SiC_2	4980	<10	KLEMAN (1956)
NH_2	5693	<5	RAMSAY (1957); DRESSLER and RAMSAY (1959)
C_3	4050	<2	GAUSSET, HERZBERG, LAGERQVIST, and ROSEN (1965)

it is necessary to verify that the same conclusions hold under these different conditions. No attempt was made to change their basic theory, but their rate coefficients were altered in the following respects. (i) In the case of CH a modern absolute f-value replaced BATES and SPITZER's estimate, and the proper adjustments were made in the γ's. (ii) The value of the radiation density enters directly into the photoionization and photodissociation rates, so the β's have been corrected by the ratio between the BATES-SPITZER radiation field density at the threshold wavelength and that of the field near ζ Oph. It was necessary (iii) also to recalculate the photoionization corrections for atomic carbon in this latter radiation field, since the concentrations $n(C^\circ)$ and $n(C^+)$ enter directly into the radiative recombination rates of CH and CH^+. The Γ's for neutral carbon were calculated from eq. (8) by use of the theoretical cross-sections given by SEATON (1958); the recombination coefficient α was taken directly from SEATON (1951). At 20 pc from ζ Oph, it is found for example that $\Gamma/\alpha = 84\ \mathrm{cm}^{-3}$ as compared to the value of $1.7\ \mathrm{cm}^{-3}$ used by BATES and SPITZER. The a_λ's calculated for the ground state of carbon by PRADERIE (1964) lead to values of Γ about 75 % higher.

The results for a particular set of assumptions[12] are shown in Table 14, where the "observed" n's are N(CH) from Table 3 divided by the appropriate layer thicknesses of Table 6. The numbers in col. 4, Table 14 show that the observed CH concentration is still 30 to 40 times higher than calculated. If the ζ Oph data had been represented by a conventional density of $n(\mathrm{H}) = 20\ \mathrm{cm}^{-3}$ at 20 pc from the star rather than with $n(\mathrm{H}) = 730\ \mathrm{cm}^{-3}$, then the discrepancy between prediction and observation for CH would have been by a factor of 2×10^4 rather than about 40.

The present discrepancy by a factor 30—40 could be reduced by assumption of a density concentration toward the layer center, since the molecular association rate is proportional to the square of the local density. It does not seem meaningful to pursue such speculative details at the present time. The significant point is that the gap between theory and observation has now been narrowed to the place where 2-body radiative recombination must again be considered seriously as a mechanism for molecule formation under interstellar conditions. It will be necessary now to reexamine the complete theory with the aim of improving the reaction rates before one can decide whether this process is a dominant one.

It must be pointed out that the present calculations do not remove a serious discrepancy between the predicted and observed $n(\mathrm{CH}^+)/n(\mathrm{CH})$ ratios that was encountered by Bates and Spitzer. The present prediction (Table 14) is that the concentration of CH^+ should be 80 to 150 times higher than that of CH. Yet if $f_{el}(\mathrm{CH}^+)$ is as expected, approximately the same as that for the stronger electronic systems of CH (Bates and Spitzer, 1951), then the concentrations of CH^+ and CH in front of ζ Oph must be of the same order of magnitude. The theoretical prediction that $n(\mathrm{CH}^+) \gg n(\mathrm{CH})$ arises largely from the fact that the photodissociation rate estimated for CH by Bates and Spitzer is about 100 times that of CH^+, which in turn rests largely on the belief that while CH can be photodissociated by photons of energy near 10 ev, CH^+ requires energies of 14 ev which lie beyond the Lyman limit where the energy density is much lower. The existence of this discrepancy is one of the major difficulties of the 2-body recombination hypothesis. It may be no more than the result of some neglected spectroscopic effect, or of an unexpectedly small f-value for CH^+, or it may mean that the hypothesis itself is untenable. Until this matter is settled, one ought not to place great confidence in the detailed results of recombination calculations such as those made here.

Finally, mention should be made of another possible origin for the interstellar molecules, namely that they are the fragments of more complex molecules which have in turn been derived from the interstellar solid

[12] For the layer at 20 pc from ζ Oph, the rate coefficients took the following values: $\alpha_1 = 7 \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$, $\beta_1 = 2.6 \times 10^{-10}\ \mathrm{sec}^{-1}$, $\beta_2 = 1.3 \times 10^{-10}\ \mathrm{sec}^{-1}$, $\beta_3 = 1.5 \times 10^{-12}\ \mathrm{sec}^{-1}$, γ_1 (non-adiabatic case) $= 3 \times 10^{-18}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$, γ_1 (adiabatic) $= 9 \times 10^{-18}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$, γ_2 (non-adiabatic) $= 3 \times 10^{-18}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$.

particles. BATES and SPITZER considered this hypothesis in an attempt to explain the anomalously strong CH^+ lines in the Pleiades as a result of photodissociated CH_4 streaming past the cluster. The difficulty in testing this hypothesis is that, of the chain of products extending between CH_4 and $C^+ + H$, only the resonance lines of CH and CH^+ are optically accessible. The situation is somewhat more favorable spectroscopically for NH_3 if it were present in space[13], because lines of NH_2 (RAMSAY, 1957), NH (Table 11), and NH^+ (COLIN and DOUGLAS, 1968) all occur at accessible wavelengths. None of these lines are found in ζ Oph, or in any other star examined.

The molecule HCN, the most obvious progenitor of CN, has no lines in the optical region. But if CN were a fragment of a still more complex molecule, one might expect that intermediate triatomic products may be found in stars where CN is strong. Electronic transitions of CNC, CCN and NCN arising from the ground state are optically accessible, and although no f-values are known, good structural analyses of the spectra are available. None of these molecules have been detected in ζ Oph. The triatomic molecules that have been sought with negative results are listed in Table 15, together with upper limits on their equivalent widths. The absence of these molecules does not rule out the hypothesis since it is possible that the lifetimes of such intermediate products are short in the interstellar radiation field. Laboratory investigation would be required to establish whether this possibility is reasonable.

5. Lithium and Beryllium

At least one T Tauri star appears projected against the ζ Oph H II region, and a large number are associated with the dark material in the denser part of the Sco-Oph complex, about 12° south of ζ Oph. The T Tauri stars as a group are abnormally abundant in Li (although none of the stars in this particular area have been examined for Li). Hence a determination of the Li content of the interstellar material in this region could bear directly upon the question whether the Li in the T Tauri stars was present in the material from which they formed, or was produced later. This was one of the incentives for studying the interstellar spectrum of ζ Oph. It was felt that information on Li derived from interstellar lines in ordinary, distant stars in low galactic latitude was not very relevant to this question, because star formation is not now taking place in the thin, nearly transparent clouds that contribute to the interstellar lines in such spectra.

The mean $(Li^6 + Li^7)/Si$ abundance in chondritic meteorites is $45. \times 10^{-6}$, which leads to the predicted N(Li I) and N(Li II) values in Table 6. The only accessible interstellar Li I line is λ 6707, a doublet having the stronger

[13] However, if NH_3 were frozen in the grains it would probably remain so: CH_4 would sublime at about 30° K, but NH_3 not until about 80° K.

$^2S_{1/2} - {}^2P^\circ_{3/2}$ component of Li^7 at 6707.761 Å, and the weaker $^2S_{1/2} - {}^2P^\circ_{1/2}$ line at 6707.912 Å. The corresponding lines of Li^6 are displaced 0.158 Å to longer wavelength. With the spectroscopic resolution used here, this structure would probably appear as a single diffuse line if blurred by $b = 2$—3 km/sec. No line can be seen near this wavelength on 4 Å/mm spectrograms of ζ Oph, and it is estimated therefore that $W^{(\lambda)} < 6$ mÅ, which leads to $N(\text{Li I}) < 1.9 \times 10^{10}$ cm^{-2}. The models of Table 6 predict $N(\text{Li I}) = 2.2 \times 10^9$, so an upper limit on interstellar Li in this direction of about 9 times the chondritic abundance is indicated.

Most determinations of stellar Li abundances have been differential with respect to the sun, and thus are based on some assumption as to the equivalent width of λ6707 in the sun. The work of Bonsack and Greenstein (1960) on T Tauri stars and of Herbig (1966) on FU Orionis contain the assumption (now known to be incorrect) that $W^{(\lambda)}_\odot(\lambda 6707) = 3.7$ mÅ. According to Peach (1967), a value of $W^{(\lambda)}_\odot(\lambda 6707) = 0.61$ mÅ corresponds to a solar abundance of $N(\text{Li})/N(\text{H}) = 2.4 \times 10^{-12}$. From this and the assumption that in the sun $N(\text{H})/N(\text{Si}) = 2.6 \times 10^4$, a solar equivalent width of 3.7 mÅ corresponds to $N(\text{Li})/N(\text{Si}) = 0.38 \times 10^{-6}$. On this basis, the Li/Si abundance in the T Tauri stars and similar objects that have been analysed ranges from about $30. \times 10^{-6}$ to $150. \times 10^{-6}$. These values are to be compared with the interstellar upper limit obtained here, $< 390. \times 10^{-6}$. Probably these numbers are not trustworthy to within factors of 2 or 3. Clearly, no decision is yet possible on the question whether the abundance of interstellar Li is compatible with the Li abundance in T Tauri stars.

The resonance doublet of Be II corresponding to Li I λ6707 occurs at 3130.42, 3131.06 Å. Several good 2.0 Å/mm spectrograms cover the region, but no line is detectable with certainty at that wavelength. The same considerations that were used to set an upper limit on the nearby OH lines lead to $W^{(\lambda)} < 2.5$ mÅ for Be II λ3130. Therefore $N(\text{Be II}) < 8.3 \times 10^{10}$ cm^{-2}. The chondritic Be/Si ratio of 0.69×10^{-6} leads to predicted values of $N(\text{Be II})$ ranging from 1.5×10^{10} to 2.1×10^{10} for the models in Table 6. Therefore the observational upper limit on the interstellar abundance of Be in the foreground of ζ Oph is 4 to 6 times the chondritic value. An improvement in the threshold of detection by an order of magnitude might produce a positive result.

There is thus no evidence for an underabundance of interstellar Be. Earlier data on the Be/Na abundance ratio in meteorites led Spitzer and Field (1955) to suspect that Be, like Ca, might be depleted insofar as it is detectable in interstellar absorption. However, more recent data on chondrites show that those analyses of Be were too high by a factor of about 30 (Sill and Willis, 1962), and the interstellar anomaly vanished when this correction was made.

6. Conclusions

It is worthwhile to list what appear to be the salient results of this investigation.

(1) A central hypothesis of the analysis is that the interstellar abundance of Na with respect to H has its solar system value. Given this, the optical interstellar line spectrum of ζ Oph having a displacement of —15 km/sec is found to originate in a thin H I sheet, having a thickness of 0.15 pc and a density of $n(\mathrm{H}) \approx 500$ to $900\ \mathrm{cm}^{-3}$, which may cover a region about 50 pc across. This sheet of neutral material is reminiscent of the similar structures that have been proposed by Heiles (1967) to account for some of his 21-cm results. The contribution of the H II region around ζ Oph and of the "intercloud medium" to the lines in the optical region are relatively small, especially for neutral atoms (Sec. 3).

(2) The abundance of K is normal, but Ca is deficient by a factor of about 1400, and Ti is also underabundant by a factor of at least 100 (Sec. 3). Explanation of these deficiencies is a major and pressing problem.

(3) Li and Be are not detected, but this is not surprising because the upper limits on their abundances set here correspond to 9 and 4—6 times, respectively, their concentrations in chondrites (Sec. 5).

(4) The atomic concentrations in the dense H I layer are high enough that it is possible that 2-body radiative recombination may be significant as a means of forming diatomic molecules. The observed low abundance of OH and particularly NH with respect to CH, CH^+ and CN are understandable if this mechanism predominates, while these selectivities are not expected if molecule formation has taken place on graphite surfaces. No triatomic molecules that might be progenitors of CN have been found in ζ Oph, despite specific search (Sec. 4).

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