

ON THE ABSORPTION CONTINUUM OF THE NEGATIVE OXYGEN ION

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ABSTRACT

A new determination of the electron affinity of oxygen (3.07 e.v.) suggests that the ionization continuum of O^- in the photographic ultraviolet region becomes so strong in late K and M stars that its contribution to the monochromatic absorption coefficient cannot be neglected. The influence of O^- on the Rosseland mean is insignificant. A discontinuity in the spectra of M giants, first observed by Lindblad, is tentatively identified with the absorption edge of O^- near λ 4050. The theoretical strength of the Lindblad discontinuity depends on the abundance ratio of atomic oxygen to atomic hydrogen, which in M stars varies with the pressure-sensitive shift of the dissociation equilibrium of the several hydrides and oxides. The result is a positive absolute magnitude effect for the Lindblad discontinuity. The differential of free-oxygen abundance implied by Lindblad's spectrophotometric observations agrees as to order of magnitude with that predicted by Russell from the dissociation equilibrium in giant and dwarf stars of the oxygen branch.

The stability of the negative ion of atomic oxygen has long been known from its frequent appearance in the mass spectrograph. From an analysis of experiments on electron collisions in molecular oxygen, W. W. Lozier¹ assigned to the oxygen atom an electron affinity of 2.2 ± 0.2 e.v. This figure warranted the conclusion that the negative oxygen ion could be dismissed as of little consequence for the continuous absorption coefficient of stellar atmospheres. Recently D. T. Vier and J. E. Mayer² have announced a considerably higher value for the electron affinity of oxygen, viz., 3.07 ± 0.08 e.v. The authors are unable to advance any explanation of the divergence of this figure from Lozier's smaller one. However, they place great confidence in their experimental method, which had previously been applied, by Mayer and several collaborators, to the various halogens and had given consistent results. Accepting the verdict of Vier and Mayer, it appears that in the late-type stellar atmospheres the continuous absorption in the photographic ultraviolet region contributed by the negative oxygen ions approaches that of the negative hydrogen ions and may even overtake the latter for the M stars. This surmise rests on a comprehensive discussion of the structure and of the absorption coefficient of O^- given by D. R. Bates and H. S. W. Massey.³ The following remarks are necessarily of a tentative nature and are mainly intended to stress the astrophysical importance of a more detailed study of the negative oxygen ion.

The ground state of O^- has the configuration $(1s)^2(2s)^2(2p)^5$ and is a $^2P^o$ term. Lozier's experiments and later ones by H. D. Hagstrum and J. T. Tate⁴ furnished evidence of the existence in O^- of a stable excited state closely adjacent to the ionization continuum. The nature of this state, whose configuration may be either $(1s)^2(2s)^2(2p)^6$ or $(1s)^2(2s)^2(2p)^4(3s)$, has been debated at length by Bates and Massey. Although they could not decide between the two possibilities, they favor the second assumption. For the computation of the ionization equilibrium in first approximation the existence of this excited state may be disregarded. The Saha equation for O^- then reads:

$$\log_{10} \frac{p_{O^0} \cdot p_e}{p_{O^-}} = -3.07 \frac{5040}{T} + 2.5 \log_{10} T - 0.48 + \log_{10} \frac{2 \cdot 9}{6}.$$

¹ *Phys. Rev.*, **46**, 268, 1932.

² *J. Chem. Phys.*, **12**, 28, 1944.

³ *Phil. Trans. R. Soc., A*, **239**, 269, 1943.

⁴ *Phys. Rev.*, **59**, 354, 1941.

The last two terms practically cancel, 9 and 6 being the statistical weights in the ground state of O and O^- , respectively. Writing the Saha equation for H^- with L. R. Henrich's⁵ new value of the electron affinity,

$$\log_{10} \frac{p_H \cdot p_e}{p_{H^-}} = -0.75 \frac{5040}{T} + 2.5 \log_{10} T + 0.12,$$

the abundance ratio of the negative ions of oxygen and hydrogen is found to be

$$\log_{10} \frac{p_{O^-}}{p_{H^-}} = \log_{10} \frac{p_O}{p_H} + 2.32 \frac{5040}{T} + 0.12 = \log_{10} A + B(T).$$

The abundance ratio A (by numbers of atoms) is not known with great accuracy, but $A = 10^{-3}$ may be regarded as a conservative estimate.⁶ Strictly speaking, A is not the abundance ratio of oxygen to hydrogen, as commonly understood, but the ratio of atomic oxygen to atomic hydrogen. This distinction becomes important at the lowest temperatures encountered in stellar atmospheres, at which the numbers of free atoms are appreciably reduced by molecular association. The table below gives for two different values of A the $\log_{10}(p_{O^-}/p_{H^-})$ and reveals how with decreasing temperature the abundance of O^- overtakes that of H^- , equality being attained approximately at $T = 4000^\circ \text{K}$ with $A = 10^{-3}$, and even at solar temperature, on the perhaps rather extreme assumption of $A = 10^{-2}$. It should be noted that this effect is independent either of the electron pressure or of the total pressure but that it is a function of A and T only.

5040/ T	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
$T^\circ \text{K}$	8400	6300	5040	4200	3600	3150	2800	2520
$B(T)$	+1.51	+1.98	+2.44	+2.90	+3.37	+3.83	+4.30	+4.76
$\log_{10} \frac{p_{O^-}}{p_{H^-}} \left\{ \begin{array}{l} A=10^{-3} \\ A=10^{-2} \end{array} \right.$	-1.49	-1.02	-0.56	-0.10	+0.37	+0.83	+1.30	+1.76
	-0.49	-0.02	+0.44	+0.90	+1.37	+1.83	+2.30	+2.76

Figure 1 reproduces the absorption coefficients (absorption cross-sections per ion) of H^- and O^- according to Henrich and to Bates and Massey, respectively. In O^- the existence or otherwise of a stable excited state belonging to the configuration $(1s)^2(2s)^2(2p)^4(3s)$ has a pronounced influence on the processes of electron capture by the oxygen atom and of photoelectric ionization of the negative ion. For details the memoir of Bates and Massey should be consulted. They give two curves for the absorption coefficient, marked A and B , corresponding to different assumptions as to the nature of the excited state. As their computations were based upon an electron affinity of 2.2 e.v., it was necessary to transform their results to the new value of 3.07 e.v., using formula (19) of their paper. Since the original data were available only in the form of graphs, no great accuracy can be claimed for this procedure, but Figure 1 is believed to be sufficiently illustrative. Approaching the ionization limit of O^- (near λ 4050) from the ultraviolet, the absorption coefficient tends to zero in case A , while it remains finite in case B (the original graph B contradicts the statement, made by Bates and Massey in the text, that the absorption cross-section tends to infinity as the frequency tends to the value at the ionization limit; but the origin of this discrepancy remains obscure). Hence, in case B we would expect to observe in stellar spectra near λ 4050 a rather conspicuous discontinuity not unlike the one at the Balmer limit, provided that the fraction p_{O^-}/p_{H^-} is much greater than 1—say, perhaps, greater than 5. In case A the rise of the O^- curve toward ultraviolet would

⁵ *A p. J.*, 99, 59, 1944.

⁶ A. Unsöld, *Zs. f. A p.*, 21, 76, 1941.

reduce the decline of the H^- curve, and at a short distance from the ionization limit a strong absorption continuum would result for, say, p_{O^-}/p_{H^-} greater than 10, i.e., at temperatures lower than about 3000°K . These inequalities are subject to a moderate upward revision, because Henrich's absorption coefficient of H^- is believed to be systematically too small from $\lambda 4000$ toward the ultraviolet. The physical mechanism distinguishing case *B* is a resonance phenomenon arising when a $(2p)^4(3s)^2P$ level of O^- exists with zero binding energy relative to the 3P normal state of the oxygen atom. Whether or not this state of affairs actually prevails in the negative ion is of no great consequence for the interpretation of M-type spectra, as proposed below. The principal difference con-

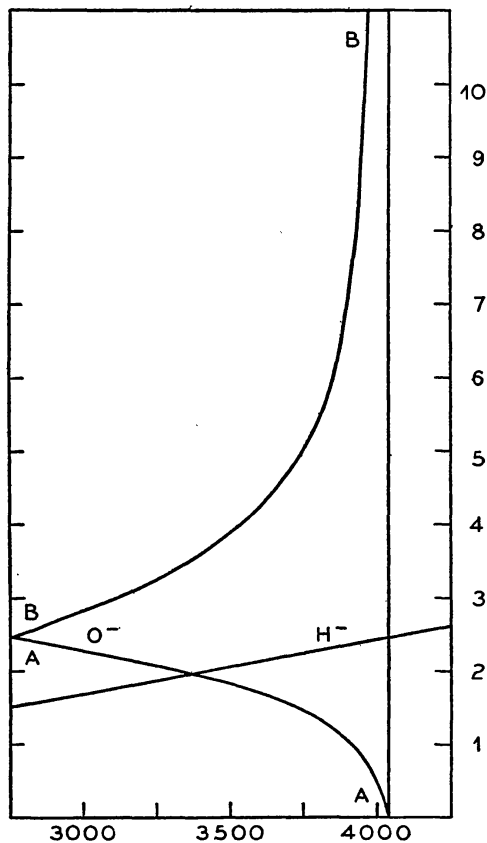


FIG. 1.—Ordinates: absorption cross-sections per ion; H^- unit 10^{-17} cm^2 , O^- (*A* and *B*) unit 10^{-18} cm^2 . Abscissas: angstrom units.

sists in the greater relative abundance of oxygen required in order to produce the O^- continuum in case *A*, for which, moreover, the absorption edge at $\lambda 4050$ would be less sharply defined than in case *B*.

B. Lindblad⁷ made a spectrophotometric comparison between $\lambda 5100$ and $\lambda 3700$ of the two M stars HD 95735, dM2, and HD 120933, gM2. His monochromatic magnitude differences (including an arbitrary zero-point correction of 0.12 mag.) are plotted in Figure 2 on a $1/\lambda$ scale, and some similar data by Y. Öhman⁸ are added to cover completely the blue-green region of the spectrum. This permits the disturbing influence of

⁷ *Stockholm Obs. Ann.*, 12, No. 2, 1935.

⁸ *Stockholm Obs. Ann.*, 12, No. 8, 1936.

the MgH bands in the dwarf to be eliminated. A straight line is drawn through Öhman's undisturbed points, representing the relative spectrophotometric gradient, namely,

$$0.921 \frac{d(m_d - m_g)}{d \frac{1}{\lambda}} = \frac{c_2}{T_d} - \frac{c_2}{T_g} = -0.55.$$

A parallel translation of Öhman's gradient, so as to fit Lindblad's points near λ 4500, reveals a strong absorption continuum in the giant, extending from about λ 4100 far into

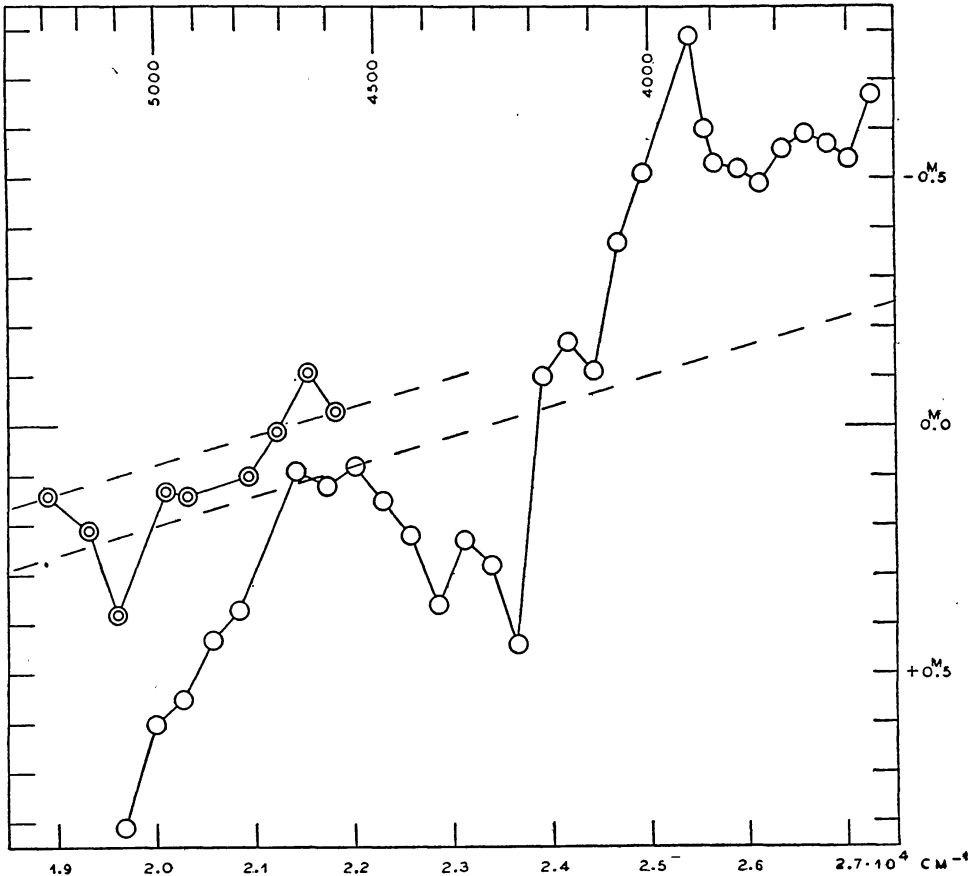


FIG. 2.—Ordinates: magnitude differences ($dM_2 - gM_2$), according to Lindblad (*op. cit.*, Table 6, represented by single circles) and to Öhman (*op. cit.*, Table 6, represented by double circles). Abscissas: wave numbers (cm^{-1}).

the ultraviolet. That this is not an isolated instance is qualitatively demonstrated by a series of low-dispersion spectrograms of 12 M dwarfs and 16 M giants, which were obtained with quartz optics at the aluminized 60-inch Mount Wilson reflector.⁹ On these spectrograms it was an easy matter to separate the giants from the dwarfs, on account of a striking difference in the appearance of the ultraviolet continuum. In the dwarfs the photographic density of the continuous spectrum steadily and slowly decreases from a maximum in the blue toward the ultraviolet limit; in the giants there is a marked drop between λ 4100 and λ 4000, or so, and no further recovery at shorter wave lengths down to λ 3300, where the spectra fade out. From exposure ratio scales it was estimated that

⁹ R. Wildt, *Ap. J.*, **84**, 335, 1936; *Mt. W. Contr.*, No. 551.

the discontinuity near $\lambda 4000$ is of the order of 0.5 mag., a figure that agrees well with Lindblad's photometry. All these spectra were photographed on infrared sensitive plates, and from the strength of the simultaneously recorded infrared maximum, near $\lambda 8500$, it was possible to estimate a crude color equivalent. Several pairs of dwarfs and giants, selected for equal apparent visual magnitude, proved to have nearly the same integrated infrared intensity but were readily distinguished by the weakness of the ultraviolet in the giants. This was taken to indicate that the surface temperatures of these pairs do not differ markedly and that a peculiar absorption mechanism located in the atmospheres of the giants is responsible for their low ultraviolet intensities. Unfortunately, similar observations of pairs of K stars were not undertaken at that time. While this sample of M stars actually investigated is admittedly small, it may be regarded as representative of the M stars at large, pending evidence to the contrary. In other words, what may be called, for sake of brevity, the "Lindblad discontinuity" and the "Lindblad continuum" are assumed to be typical features of the giant M spectra.

The relation between color and effective temperatures observed among G and F stars cannot, as yet, be predicted from theory, though steady progress in this direction has been made through the efforts of Williamson and Henrich. This problem will be even harder to solve for the K and M stars, because of purely observational difficulties. In their spectra the crowding of lines and bands makes it exceedingly difficult to define clearly what should be regarded as continuous background, but this dilemma can perhaps be circumvented by differential spectrophotometric observations of dwarfs and giants having the same spectral type. Such observations, i.e., of the very sort Lindblad and Öhman have carried out, should eliminate in the first approximation the disturbing influence of the line and band absorption and, therefore, should lend themselves to a test of the theory of the continuous absorption coefficient by way of the absolute-magnitude effects it implies. Now, according to the current theory of the atmospheric absorption coefficient, for temperatures lower than 5000° K the contribution of atomic hydrogen to the opacity becomes negligibly small and the parameter, k_ν/\bar{k} , which determines the intensity distribution in the continuum, is a function only of the temperature, since for H^- both k_ν and \bar{k} are proportional to the electron pressure. Consequently, the relative spectrophotometric gradient, dwarf *minus* giant, should be a function only of the difference of the effective temperatures, which are marked among the K stars and seem to disappear at M0, according to G. P. Kuiper's¹⁰ study of the temperature scale. On the other hand, the difference in color temperature between K dwarfs and giants to be expected on the current theory ought to be small, on account of the slight dependence of the variation of k_ν/\bar{k} with temperature in the relevant range. But the observed differences in color temperatures between dwarfs and giants are considerable for late G and K stars, and this throws some doubt on the adequacy of the current theory, operating with H^- as the only source of continuous absorption.

With the recognition of the Lindblad discontinuity as a typical feature of the M giants in general, it becomes practically certain that another absorption mechanism besides the photoelectric ionization of H^- must be introduced for these stars into the theory of the continuous spectrum. The tentative identification of this new agent with the negative ion of atomic oxygen seems natural at this stage. While the final test of this conjecture must await a quantum mechanical analysis of the structure of O^- going beyond the work of Bates and Massey, some astrophysical consequences of the proposed identification will be taken up here. With H^- and O^- operating jointly, the parameter k_ν/\bar{k} would still be independent of the electron pressure. Therefore, no Lindblad discontinuity could appear in the giants, because the dwarfs and giants of the early subdivisions of class M are supposed to have nearly the same effective temperatures, unless oxygen were much more abundant in the giants than in the dwarfs. The giants are now widely held to be a cosmogonically distinctive group of stars, and there is no a priori reason to reject the hy-

¹⁰ *Ap. J.*, **88**, 429, 1938.

pothesis that they might be richer in oxygen than the main-sequence stars. Fortunately, there is no need to rely on this rather special hypothesis. It is mentioned here merely because a true cosmic difference in abundance may be superimposed upon, and hard to disentangle from, an apparent difference in the abundance of free atomic oxygen, such as is bound to result from the greater amount of oxygen that is locked up in molecules in the M dwarfs, in consequence of their higher mean atmospheric pressure. This effect is very conspicuous in H. N. Russell's¹¹ diagrams illustrating the shift of the dissociation equilibrium as function of the atmospheric temperature, both for giant and for dwarf stars. According to Russell's graphs, the abundance factor $A = p_O/p_H$, as used above, is constant in the giants at temperatures higher than 2500° K. But in the dwarfs, A has fallen at 2800° K to one-tenth of its value at 3150° K, above which temperature it is constant. This means that with decreasing temperature the giants become relatively richer in free atomic oxygen. Conversely, the dwarfs become poorer in negative oxygen ions. Of course, Russell's figures are subject to change on altering the composition of the model atmosphere, but the qualitative characteristics of his diagrams are expected to be conserved. The differential of oxygen abundance required to produce a Lindblad discontinuity of 0.5 mag. can be estimated with the help of G. Burkhardt's¹² table, which gives the monochromatic flux averaged over the stellar surface as function of the two variables k_ν/\bar{k} and $h\nu/kT_e$. Regarding case *A*, with $T_e = 3150^\circ$ K and $A = 10^{-3}$ for the dwarfs, it seems that A would have to be larger by a factor of the order of 5 in the giants. For case *B* the absorption of O^- near the ionization limit is so much stronger that a smaller A could be chosen for the dwarfs, and yet in the giants the required oxygen abundance would have to be greater by a small factor only, perhaps of the order of 2. No great precision can be attained in making these estimates, among other reasons because the choice of the correct value for \bar{k} is a matter of some difficulty, as will be explained presently. Notwithstanding that, it appears safe to say that the interpretation of the Lindblad discontinuity proposed here does not imply an unreasonably large difference in oxygen abundance between giants and dwarfs. Incidentally, it may be noted that the influence of O^- on the computation of \bar{k} is quite insignificant, since the frequency dependent weight factor entering the Rosseland mean is small in the ultraviolet.

In order to make the estimates just described, \bar{k} was computed for $T = 3150^\circ$ K by adding the absorption coefficients for the bound-free (Henrich) and free-free (Wheeler and Wildt) transitions of H^- , with the result $\bar{k} = 0.95 \cdot 10^{-18}$ cm² (this is the Rosseland mean of the absorption cross-section, not the mass absorption coefficient). This figure is predominantly determined by the high transparency to the infrared side of the ionization limit of H^- , as will be apparent from the nature of the Rosseland mean as a harmonic mean. Specifically, k_ν/\bar{k} assumes the values of 7.5 and 0.15 at the frequencies 7000 and 6000 cm⁻¹, respectively, which would entail an immensely strong emission on the infrared side of the ionization limit of H^- . Burkhardt's table does not extend beyond $k_\nu/\bar{k} = 0.5$, but it can be inferred that near λ 16,000 the energy-curve of the M stars should rise steeply toward the infrared by many magnitudes. This conclusion is certainly contradicted by the few known infrared energy-curves of late-type stars,¹³ though the resolving-power of these measurements was rather small. This, then, brings to light a serious deficiency of the present theory of the continuous absorption coefficient, as far as the low-temperature range is concerned. There does not seem to exist any grave "infrared problem" at solar temperatures. For the contribution of the free-free transitions of H^- varies ever so little with temperature, while the absorption from bound-free transitions mounts rapidly with falling temperature. In order to stop this infrared leakage at low temperatures, some new absorption mechanism affecting primarily the infrared would have to be found. Further

¹¹ *Ap. J.*, 79, 281, 1934; *Mt. W. Contr.*, No. 490.

¹² *Zs. f. Ap.*, 13, 56, 1936.

¹³ C. G. Abbot, *Ap. J.*, 69, 293, 1929.

discussion of this point would go beyond the scope of this paper, but it is well to remember that the free-free absorption coefficient of H^- has been derived from an approximate theory.

Finally, the splitting of the giant branch into two parallel sequences—the oxygen and the carbon stars—is of particular interest in the context considered here. The study of the low-dispersion spectra of 16 carbon stars⁹ disclosed an important difference between the spectral classes R and N as regards their ultraviolet continuum, which is very strong in the former and excessively weak in the latter (for the prototype, 19 Piscium, it was estimated from exposure ratio scales that the energy-curve drops by about 2.5 mag. near λ 4000).¹⁴ These observations lead to some speculations on the atmospheric opacity of late-type stars, in so far as it is caused by continuous molecular absorption. It is now necessary to re-examine this situation with reference to the continuous absorption produced by negative ions, but such an attempt would be unprofitable at this time for lack of many requisite data. The negative ion of atomic carbon appears with great strength in the mass spectrograms. Quantum mechanical estimates have indicated for carbon an electron affinity of about 1 e.v. However, this result may be off by 100 per cent or more, as experience from similar computations for other negative ions has taught.

¹⁴ A further factor which may be of importance in this connection is the systematic difference of temperature which appears to exist between the R and the N stars (cf. P. C. Keenan and W. W. Morgan, *Ap. J.*, **94**, 501, 1941).