### CONTINUOUS SPECTRA

#### GEORGE H. SHORTLEY

After a brief review of the definitions and formulae for such quantities as line strengths, oscillator strengths, and transition probabilities in the case of discrete-discrete transitions, the corresponding quantities were defined for the case of continuous emission and absorption. By placing the atom or molecule at the center of a large spherical box, the proper normalization of the radial wave functions to use in the continuous spectrum was obtained. This is such that the asymptotic form for large r of the function with energy E is

$$\frac{1}{\sqrt{\hbar\pi}} \sqrt[4]{\frac{2\mu}{E}} \sin \sqrt{\frac{2\mu E}{\hbar}} (r - \delta) .$$

With this normalization the radiation probabilities refer directly to unit energy range in the continuous spectrum. Photoionization, autoionization, and predissociation were discussed. Then a new method of calculating the relative probabilities of transitions into the various levels of an atomic configuration in the case of electron capture by an ion was reported. These calculations were made with D. H. Menzel to furnish a possible explanation of peculiar intensities in the nebular spectra, but they have not been successful in this direction. The methods of calculation will be discussed in a note in the Astrophysical Journal in the near future.

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## ELECTRON AFFINITY IN ASTROPHYSICS

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The carriers of the emission and absorption spectra observed in celestial objects have been identified as both neutral and positively charged atoms and molecules. A number of free electrons, equivalent to the charge of the positive ions, must be present to provide for electric neutrality. Collisions between electrons and certain neutral atoms or molecules should frequently lead to attachment, a negatively charged atomic or molecular ion being formed. The existence of such negative ions has been demonstrated by a great variety of experiments, among which the analysis of ionic beams in a mass

spectrograph affords the most direct evidence; and their stability is also accounted for by atomic theory.

Although it has long been recognized that negative ions play an important role in the Kennelly-Heaviside layer of the terrestrial atmosphere, their presence in stellar atmospheres does not seem to have been envisaged. Several species of neutral atoms and molecules, abundant in stellar atmospheres, are able to attach electrons in stationary states. This tendency to attach electrons is generally re-

TABLE 1
ELECTRON AFFINITIES

Atom and Ground State	I.P.	E.A.	References
1 H <sup>2</sup> S	13.53	0.70	E. A. Hylleraas, Zs. f. Phys., 65, 209, 1930
3 Li <sup>2</sup> S	5.37	0.54	Ta You-Wu, Phil. Mag., 22, 837, 1936
8 O <sup>3</sup> P	13.55	2.2	W. W. Lozier, Phys. Rev., 46, 268, 1932
9 F <sup>2</sup> P	17.34	4.13	J. E. Mayer and L. Helmholz, Zs. f. Phys., 75,
16 S 3P	10.31	2.8	J. E. Mayer and M. Maltbie, Zs. f. Phys., 75, 748,
17 <i>Cl</i> <sup>2</sup> P	12.96	3·75	Mayer and Helmholz, <i>ibid</i> .  Mayer and Helmholz, <i>ibid</i> .  Mayer and Helmholz, <i>ibid</i> .
35 <i>Br</i> <sup>2</sup> P	11.80	3·53	
53 <i>I</i> <sup>2</sup> P	10.55	3·22	

ferred to, in physical and chemical literature, as "electron affinity" of the neutral particles, and the same term is used to denote the energy of binding measured in electron volts. The bond may be severed either by a subsequent collision or by photoelectric ionization. In thermodynamic equilibrium the concentration of the nega-

<sup>1</sup> A monograph on Negative Ions has just been published by H. S. W. Massey (Cambridge University Press, 1938). A letter received in March, 1939, from Dr. Massey communicates preliminary results of a new calculation of the absorption coefficients of H-. Using the Hylleraas form for the ground-state wave function instead of the former rough approximation, he finds absorption coefficients of the same order of magnitude, in the astrophysically relevant range of wave lengths, as those given by Jen (Phys. Rev., 43, 540, 1933), to which reference has been made in a brief note to appear soon in the Publications of the American Astronomical Society. Utilizing Jen's data, it has been shown that the addition of the  $H^-$  absorption to the metallic absorption produces for the solar atmosphere that desired independence of the absorption coefficient from wave length which failed to emerge from Unsöld's and Pannekoek's theory. In the opinion of the writer this result is not likely to be changed materially when Jen's data eventually will be replaced by Massey's improved data. This would mean the removal of a serious discrepancy between theory and observation and, in fact, the identification, by their continuous absorption spectrum, of the negative hydrogen ions so abundant in the solar atmosphere.

tive ions is ruled by the general principles of statistical mechanics and can be evaluated numerically from the Saha equation, in which the electron affinity has to be substituted for the ionization potential. The number of reliably determined electron affinities is still very small, as will be seen from Table 1. Many astrophysically important diatomic molecules are known to form negative ions, like  $H_2$ ,  $C_2$ ,  $O_2$ , NH, OH, CN, and others; but there is scarcely any information available about the respective electron affinities. On inspecting Table 1 it will be noticed that all the electron affinities are small compared to the ionization potentials of the corresponding atoms. This circumstance counteracts the formation of negative ions in a system consisting of a single sort of atoms only, because at any temperature high enough to release electrons by ionization of the neutral atoms the negative ions would split up even more. However, in a mixture of two atoms differing greatly in ionization potential say sodium and hydrogen—the electrons released from the sodium atoms at comparatively low temperatures may readily attach themselves to the hydrogen atoms. This is just the case realized in stellar atmospheres of medium or late spectral type. In addition, the great abundance of hydrogen will favor the formation of  $H^-$  ions. Therefore, the  $H/H^-$  equilibrium suggests itself as the most promising subject of an inquiry into the astrophysical significance of electron affinity.

If the pressure is measured in dynes per square centimeter, the Saha equation of the  $H/H^-$  equilibrium assumes the form

$$\log_{10} K = \log_{10} \left( \frac{P_H \cdot P_e}{P_{H^-}} \right) = -\frac{0.70 \cdot 5040}{T} + 2.5 \log_{10} T + 0.12$$

the statistical weight of  $H^-$  being 1. The ratios  $P_{H^-}/P_{H}$  were computed as functions of the electron pressure and temperature, and for sake of comparison there are also given the ratios of the numbers of neutral hydrogen atoms in the second and first quantum state,

$$\frac{N_2}{N_1} = 4 \cdot 10^{-\left(\frac{10.16 \cdot 5040}{T}\right)}.$$

Table 2 contains these quantities as functions of the temperature and the total pressure in the "Russell-mixture" of elements.<sup>2</sup> This

<sup>2</sup> H. N. Russell, Ap. J., 75, 337, 1932.

mixture is rather rich in hydrogen. Unsöld's analysis of the vertical distribution of temperature and electron pressure throughout the solar atmosphere<sup>3</sup> is based on a smaller abundance ratio of hydrogen to metals and therefore is less favorable to the formation of  $H^-$ . Table 3 contains the same quantities as Table 2, for several optical

TABLE 2
IONIZATION EQUILIBRIUM OF NEGATIVE HYDROGEN IONS\*

$T^{\circ} K \dots 5040/T \dots \log_{10} K \dots$	8400 0.6 + 9.51	6300 0.8 + 9.06	1.0	I.2	3600 1.4 + 8.03	1.6	1.8	2.0	3.0
Total pres- sure:									
10 <sup>4</sup>	6.99 7.62								
10² 10	8.21	8.79	8.56	8.57	8.51	8.40		8.48	
I	9.83		10.48	10.20	10.19	10.18	10.02	9.92	10.54
10-2		11.48		U	11.86	11.82	11.85	11.70	11.61
10-4		13.36							-
$\log_{10} rac{N_{ m r}}{N_{ m 2}}$	5.50	7 · 53	9.56	11.59	13.62	15.66	17.69	19.72	29.88

<sup>\*</sup>The table gives  $\log_{10} (P_H/P_{H^-})$ , the total pressure being measured in dynes per square centimeter.

 $\begin{tabular}{ll} TABLE & 3 \\ NEGATIVE & HYDROGEN & IONS & IN THE SOLAR & ATMOSPHERE \\ \end{tabular}$ 

Optical Depth	5040/T	$P_{H^-}/P_H$	$N_2/N_1$
0.12	1.0	10 <sup>-7.34</sup>	10 <sup>-9.56</sup>
	0.9	10 <sup>-7.02</sup>	10 <sup>-8.55</sup>
	0.8	10 <sup>-6.87</sup>	10 <sup>-7.53</sup>
	0.7	10 <sup>-6.82</sup>	10 <sup>-6.52</sup>
	0.6	10 <sup>-6.66</sup>	10 <sup>-5.50</sup>

depths under the solar surface, and reveals the surprising fact that, in the higher levels, the negative hydrogen ions are more abundant than the neutral hydrogen atoms excited to the ground state of the Balmer series. In view of the great strength of the Balmer series in the solar spectrum, it is obvious that the negative hydrogen ions

³ A. Unsöld, Zs. f. Ap., 8, 262, 1934.

should produce conspicuous absorption lines in the medium and late spectral types if they possessed stable excited states capable of combining with the ground state.

At present, no definite answer can be given to the question whether or not there are stable excited states in negative ions. It has been established, as a general result, that their number could not be infinite, as in the case of an electron bound in a Coulomb field. The small binding energy of the attached electron in its ground state makes it most unlikely that any stable discrete excited states exist with appreciable binding energy, though there might be some states with very small binding energy, closely adjacent to the ionization continuum. With the coronal and certain interstellar lines defying all efforts of the spectroscopists at identification, it may not be untimely to remark upon the remote chance of negative ions being the carriers of these spectra. This has already been suggested, though rather perfunctorily, for the coronal lines by Goudsmit and Ta You-Wu.<sup>4</sup> This is the only reference, in astrophysical literature, to negative ions of which the writer is aware. Since the solar corona is now widely regarded, for its scattering properties, as a cloud of free electrons, it would seem to be the very place where negative ions are likely to be formed by collisions between the indigenous electrons and neutral atoms ejected from the sun during its eruptive activity. Unfortunately, there is little hope, if any, for the discovery, in the near future, of spectra of negative ions in the laboratory or for the theoretical prediction of their energy states.

The small electron affinity of hydrogen, 0.70 volt, would place any hypothetical discrete spectrum of the negative hydrogen ion far out into the infrared, beyond the ionization limit of  $H^-$ , near  $\lambda$  17600. The rapid decay of atomic ionization continua toward greater frequencies might make one expect that the continuous absorption coefficient of  $H^-$  is negligibly small throughout the visual spectral region and the near ultraviolet. But the negative hydrogen ions show a strikingly different behavior, according to an investigation by Massey and Smith, who computed the cross-sections for the capture of electrons by hydrogen atoms. Assuming thermodynamic equilibrium, these capture coefficients can easily be transformed, by Milne's formula, into cross-sections for absorption or, by a different

4 Ap. J., 80, 154, 1934. 5 Proc. R. S., A, 155, 472, 1936. 6 Phil. Mag., 47, 209, 1924.

name only, into the astrophysically relevant absorption coefficients pertaining to the bound-free transitions of the negative hydrogen ion. The absorption coefficient of  $H^-$  rises from zero, at the ionization limit, to a broad maximum at a distance of about 10 volts from the ionization limit. It then decreases gradually, extending with remarkable intensity into the region between 20 and 30 volts. Massey and Smith do not give any estimate of the accuracy of their crosssections; but it may be hoped that their results are trustworthy for the astrophysically accessible spectral range, which is rather close to the ionization limit. Menzel and Pekeris<sup>7</sup> had already computed what they call the absorption resulting from the changes of kinetic energy of an electron traversing the field of a neutral hydrogen atom. From the point of view presented here, this absorption may be described as produced by the free-free transitions of the negative hydrogen ion. The absorption coefficient  $k_{\nu}$ , resulting from the existence of negative hydrogen ions in a gas containing  $N_e$  electrons per unit volume, is, per neutral hydrogen atom,

for free-free transitions:

$$\frac{1}{3} \frac{e^2 h N_e}{c m^3 v^3} \left( \frac{m v_0^2}{2 \pi k T} \right)^{3/2} v_0^4 A(T, v_0) = a \cdot P_e,$$

and

for bound-free transitions:

$$\frac{1}{4} \frac{mc^2h(\nu - \nu^*)}{h^2\nu^2} Q^e N_e \left(\frac{h^2}{2\pi mkT}\right)^{3/2} e^{h\nu^*/kT} = b \cdot P_e.$$

The coefficients a have been taken from the paper of Menzel and Pekeris, and the coefficients b have been computed from the emission cross-sections  $Q^e$  published in the form of a graph by Massey and Smith,  $\nu^*$  being the frequency corresponding to the electron affinity of hydrogen. As will be seen from Table 4, the bound-free transitions produce an absorption far greater than that of the free-free transitions, especially at lower temperatures. Now the latter, as found by Menzel, is still negligible at the solar temperature, amounting to about 5 per cent of the metallic absorption. However, they would become appreciable at lower temperatures, particularly in dwarf

<sup>&</sup>lt;sup>7</sup> M.N., **96**, 77, 1935.

stars. Therefore, with regard to the comparison given in Table 4, it would seem that the contribution by negative hydrogen ions to the opacity of stellar atmospheres cannot be neglected altogether, even at the solar temperature. It is generally agreed that the present theory of the atmospheric absorption coefficient is unsatisfactory,

TABLE 4
ABSORPTION COEFFICIENT OF NEGATIVE HYDROGEN IONS*

T <sup>◦</sup> K	λ 8900	λ 6810	λ 5390	λ 4360	λ 3030	
3000	{ 6.82	4.12	2.70	1.88	1.04	
	{150	160	250	310	370	
4000	{ 5.81	3.41	2.20	1.50	0.81	
	37	40	62	79	94	
6000	<pre>{ 4.83</pre>	2.71	1.69	I.I2	0.55	
	6.7	7.2	11.3	I4.4	17.1	
8000	$ \left\{ \begin{array}{c} 4.33 \\ 2.3 \end{array} \right. $	2.36 2.5	1.44 3.9	0.93 5.0	0.47 5·9	

<sup>\*</sup> Upper line:  $a \cdot 10^{28}$  free-free transitions. Lower line:  $b \cdot 10^{28}$  bound-free transitions.

and to take into account this new source of opacity may help to remove the discrepancies between theory and observation, at least partly. A detailed investigation is under way.

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# MOLECULAR BANDS IN STELLAR SPECTRA

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## OBSERVATIONAL RESULTS

Bands due to diatomic molecules are the most important characteristic of the spectra of the majority of the stars. It is true that only 1.7 per cent of the total number of stars in the *Henry Draper Catalogue* belong to spectral class M, characterized by molecular bands due to the TiO molecule. This is, however, the result of observational selection, as most of the M stars are dwarfs with a very low absolute magnitude. In the sample supplied by the stars within 5 parsecs of the sun, more than 60 per cent are M-type dwarfs. On the other hand, the classes S (ZrO), N, and R  $(C_2$  and CN) are