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The Continuous Electron Affinity Spectrum of Hydrogen

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A wave-mechanical calculation has been made of the intensity distribution in the continuous emission spectrum due to the capture of electrons by normal hydrogen atoms and the coefficient of absorption in the corresponding absorption spectrum due to the neutralization of negative hydrogen ions. Approximate wave functions for the continuous range of upper energy levels have been combined with the discrete state wave function for H^- given by Hylleraas to give the matrix components for the desired transitions. The computed results are graphically illustrated and their significance discussed. It is shown that an experimental attempt to find the electron affinity emission spectrum of normal hydrogen atoms may encounter at least two difficulties: (1) insufficient intensity compared to that in experiments on the recombination between H^+ ions and electrons, and (2) spectral distribution such that the spectral limit is too diffuse for positive identification. The relation of these results to the interpretation of experiments on the electron affinity spectrum of halogen atoms is discussed.

Introduction

FOLLOWING the first proposal by Franck,[1] many attempts have been made to determine the electron affinity of electronegative elements by spectroscopic means. Certain unidentified continuous spectra have often been taken as those related with electron affinity, but such identifications have proved to be either false or uncertain.[2] The recent experiments of Oldenberg on the emission spectrum of iodine atom also point to a negative result.* A theoretical explanation for this experimental failure is obviously demanded. However, a complete answer to the problem is difficult because of the complexity of the atoms involved. As a start we propose to treat the electron affinity spectrum of the hydrogen atom, which is the simplest of such problems, and hope to furnish probable explanations for the more complicated halogen atoms.

If free electrons are present in the midst of normal hydrogen atoms, there may be a probability of combination between them to form negative hydrogen ions. The change of energy in such a transition is released as radiation, which, if spectroscopically observed, is expected to form a continuous emission spectrum extending toward the short wave-length side from an edge whose frequency is determined by the electron affinity of the atom. Conversely, a continuous absorption spectrum will be formed when negative hydrogen ions are broken up into neutral atoms and electrons under the influence of light.

The electron affinity of a hydrogen atom has been calculated by Hylleraas[3] and Bethe[4] from a general treatment of the two-electron problem. In spite of the discordant theoretical results[5] which had appeared previously and the absence of sufficient experimental data, their calculations seem to be quite definite and convincing, especially in view of the remarkable success of Hylleraas' method on other examples of the two-electron problem.[6] With the help of their characteristic wave function of a negative hydrogen ion and our present approximate solution of the wave equation in the continuous state, we shall calculate the matrix component of transition for the continuous spectrum, from which the emission intensity and absorption coefficient can be readily deduced.

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* O. Oldenberg, Phys. Rev. **43**, 534 (1933).

[1] J. Franck, Zeits. f. Physik **5**, 428 (1921).

[2] W Steubing, Ann. d. Physik **64**, 673 (1921).
O. Oldenberg, Zeits. f. Physik **25**, 136 (1924).
E. V. Angerer und Müller, Phys. Zeits. **26**, 643 (1925).

[3] E. A. Hylleraas, Zeits. f. Physik **60**, 624 (1930).

[4] H. Bethe, Zeits. f. Physik **57**, 815 (1929).

[5] L. Pauling, Phys. Rev. **29**, 285 (1927).
H. Brück, Zeits. f. Physik **51**, 707 (1928).

[6] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).

I. APPROXIMATE SOLUTION OF THE WAVE EQUATION IN THE CONTINUOUS STATE

The Schrödinger differential equation for two electrons acting in the field of a single fixed proton charge is

$$\nabla_1^2\psi+\nabla_2^2\psi+\{E_T+2(1/r_1+1/r_2-1/r_{12})\}\psi=0, \tag{1}$$

where E_T, the total energy, is measured in terms of Rh and the r's are in terms of $a=h^2/4\pi^2me^2$.

Since the above equation cannot be solved exactly by any ordinary process, we shall resort to a method of approximation. It may be assumed that the electron in the normal state of hydrogen is not appreciably disturbed by the external electron so that the interaction term is considered to affect the potential function of the latter only. Separation of variables is thus made possible.

Let

$$\psi=F_0(i)f(j), \qquad E_T=E_0+\epsilon, \tag{2}$$

where $F_0(i)$ and E_0 denote respectively the characteristic wave function and energy value of the electron belonging to the hydrogen atom in the normal state; $f(j)$ and ϵ denote respectively the continuous wave function and energy of the external electron. The letters i and j are used to designate the "inner" and "outer" electrons; either of them may be numbered as 1 and the other as 2.

Eq. (1) is then separated into

$$\nabla_i^2F_0(i)+(E_0+2/r_i)F_0(i)=0, \tag{3}$$

$$\nabla_j^2f(j)+\{\epsilon+2U(r_j)\}f(j)=0. \tag{4}$$

The normalized characteristic solution of Eq. (3) for the lowest energy level is

$$F_0(i)=\pi^{-\frac{1}{2}}e^{-r_i}. \tag{5}$$

The solution for Eq. (4) may be sought first by the usual method of separation of variables in spherical coordinates. The angular component of $f(j)$ has the usual expression $P_l^m(\cos\theta_j)e^{im\phi_j}$ while the radial component, $R_{\epsilon,l}(r_j)$, must satisfy the differential equation

$$d^2(r_jR)/dr_j^2+\{\epsilon+2U(r_j)-l(l+1)/r_j^2\}(r_jR)=0, \tag{6}$$

where l is an integer.

Now we must find an expression for $U(r_j)$, which consists of the potential energy due to nuclear attraction and the interaction energy. To a close approximation, the interaction term is the average of $1/r_{ij}$ over all the configuration space of the inner electron. The result is

$$U(r_j)=\frac{1}{r_j}-\int_{\infty}\frac{F_0^2(i)d\tau_i}{r_{ij}}. \tag{7}$$

The integral is readily carried out by expanding $1/r_{ij}$ in spherical harmonics with the result

$$U(r_j)=(1+1/r_j)e^{-2r_j}. \tag{8}$$

Even with the above expression, a direct solution for Eq. (6) is still quite difficult. However, Eq. (8) can be very roughly represented by

$$U(r_j)\sim Z^*/r_j \tag{9}$$

where Z^* is a constant (less than one in this case) and is to be interpreted as the effective nuclear number with respect to the external electron. Z^* can be adjusted to make the expression in Eq. (9) fit a limited portion of the curve represented by Eq. (8). As it will be shown later, l in Eq. (6) must be 1 by the selection rule for the transition under consideration, so that the term $l(l+1)/r_j^2$ predominates for $r_j\ll 1$. This means that we will only have to secure reasonable fitting for large values of r_j. The numerical determination for Z^* will be discussed later.

By our above assumption Eq. (6) becomes

$$d^2(r_jR)/dr_j^2+\{\epsilon+2Z^*/r_j-l(l+1)/r_j^2\}(r_jR)=0. \tag{10}$$

It is well known that the above differential equation is satisfied by the Laplace contour integral[7] which can in turn be transformed into

$$-2iR_{\epsilon,\,l}(r_j)=r_j^l\int_{-i(\epsilon)^{\frac{1}{2}}}^{i(\epsilon)^{\frac{1}{2}}}e^{\zeta r_j}(\zeta+i\epsilon^{\frac{1}{2}})^{l+iZ^*\epsilon^{-\frac{1}{2}}}(\zeta-i\epsilon^{\frac{1}{2}})^{l-iZ^*\epsilon^{-\frac{1}{2}}}d\zeta. \tag{11}$$

The solution for $f(j)$ is therefore simply the continuous wave function for the hydrogen atom with an effective atomic number Z^* instead of 1. The normalization of such a function can be carried by the method of Fues[8] as follows:

$$\int_{\infty}d\tau_jf_{\epsilon_2}^*(j)\int_{\epsilon_1}^{\epsilon_1+\Delta\epsilon_1}f_\epsilon(j)d\epsilon=1\ \text{or}\ 0 \tag{12}$$

according as $\epsilon_1<\epsilon_2<\epsilon_1+\Delta\epsilon_1$ or not. The result is identical to that of Fues:

$$f_{\epsilon,\,l,\,m}(j)=\left[\frac{(2l+1)}{2}\frac{(l-m)\,!}{(l+m)\,!}\right]^{\frac{1}{2}}\frac{e^{(3\pi/2)(Z^*/\epsilon^{\frac{1}{2}})}}{\pi[2(\epsilon)^{\frac{1}{2}}]^{l+\frac{1}{2}}|\Gamma(l+1+i(Z^*/\epsilon)^{\frac{1}{2}})|}R_{\epsilon,\,l}(r_j)P_l^m(\cos\theta_j)e^{im\phi_j}. \tag{13}$$

$F_0(i)f_{\epsilon,\,l,\,m}(j)$ is a particular solution for the wave function in the continuous state. Since i, j can be either 1, 2 or 2, 1, there are two linearly independent solutions, the proper normalized linear combinations are, of course, the symmetric and antisymmetric ones,[9]

$$\psi_{\epsilon,\,l,\,m}(\mathrm{H}^0+e)=2^{-\frac{1}{2}}\{F_0(1)f_{\epsilon,\,l,\,m}(2)\pm F_0(2)f_{\epsilon,\,l,\,m}(1)\}. \tag{14}$$

The bracket (H^0+e) is now added to denote the wave function of a normal hydrogen atom and an external electron before capture, in order to distinguish it from the discrete wave function. In the present special case, however, the characteristic wave function for H^- (see next section) is symmetric; the antisymmetric function represented by the lower sign in Eq. (14) can be omitted because it contributes nothing to the matrix component.

II. Characteristic Wave Function of H⁻ Obtained by Hylleraas

By a variational method Hylleraas[6] obtained for the lowest energy level of H^- an approximate characteristic function in the following form,

$$\psi(\mathrm{H}^-)=Ce^{-\alpha(r_1+r_2)}\{1+\beta r_{12}+\gamma(r_1-r_2)^2\}, \tag{15}$$

where α, β, γ are constants and C is the normalization constant which can readily be shown to be

$$C=\alpha^3/\pi\left[1+6\beta^2+\frac{35}{8}\frac{\beta}{\alpha}+\frac{3\gamma}{\alpha^2}+\frac{77}{8}\frac{\beta\gamma}{\alpha^3}+\frac{9\gamma^2}{\alpha^4}\right]^{\frac{1}{2}}.$$

The presence of the factor r_{12} in Eq. (15) is somewhat troublesome when we come to the integration. But we can eliminate the difficulty by the following expansion

$$r_{12}=\hat{r}\sum_{\nu=0}^{\infty}\left(\frac{x^2}{2\nu+3}-\frac{1}{2\nu-1}\right)x^\nu P_\nu(\cos\Theta), \tag{16}$$

where

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[7] L. Schlesinger, *Einführung in die Theorie der gewöhnlichen Differential-gleichungen auf funktionentheoretischer Grundlage,* § 67.

[8] E. Fues, Ann. d. Physik **81**, 281 (1926).

[9] E.g., A. Sommerfeld, *Wave Mechanics,* p. 229.

$$P_\nu(\cos\Theta)=\sum_{\mu=-\nu}^{\nu}\frac{(\nu-|\mu|)!}{(\nu+|\mu|)!}P_\nu{}^\mu(\cos\theta_1)P_\nu{}^\mu(\cos\theta_2)e^{i\mu(\phi_1-\phi_2)}, \tag{17}$$

$$\cos\Theta=\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2),$$

$\hat{r}$= larger of the two radii, r_1 and r_2; x= ratio of the smaller to the larger radius.

III. The Square of the Matrix Component of Transition

The matrix component of transition formed by $\psi_{\epsilon,\,l,\,m}(\mathrm{H}^0+e)$ and $\psi(\mathrm{H}^-)$ in the directions x, y, z of the Cartesian coordinates may be defined as

$$\left.\begin{matrix}X_{\epsilon,\,l,\,m}\\ Y_{\epsilon,\,l,\,m}\\ Z_{\epsilon,\,l,\,m}\end{matrix}\right\}=\int\!\!\int_\infty \psi^*_{\epsilon,\,l,\,m}(\mathrm{H}^0+e)\left\{\begin{matrix}x_1+x_2\\ y_1+y_2\\ z_1+z_2\end{matrix}\right\}\psi(\mathrm{H}^-)dx_1dy_1dz_1dx_2dy_2dz_2. \tag{18}$$

Let $M^2_{\epsilon,\,l,\,m}$ be the square of the amplitude of the total matrix component per unit energy range. Then the sum over all allowable values of l, m is

$$\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}=\sum_{l,\,m}\{|X_{\epsilon,\,l,\,m}|^2+|Y_{\epsilon,\,l,\,m}|^2+|Z_{\epsilon,\,l,\,m}|^2\}. \tag{19}$$

The three components can be evaulated when we transform Eq. (18) in terms of spherical coordinates and make use of the expressions derived for $\psi_{\epsilon,\,l,\,m}(\mathrm{H}^0+e)$ and $\psi(\mathrm{H}^-)$. We immediately find that $M^2_{\epsilon,\,l,\,m}$, vanishes except for $l=1$ and $m=0$ or ±1. Therefore the external electron must have an angular momentum quantum number 1 in order to have a chance to be captured by the atom.

Summing up the contributions due to the three different values of m, we arrive at the result

$$\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}=\frac{8\pi}{9}\frac{c^2}{\epsilon^{\frac{3}{2}}}\frac{e^{3\pi Z^*/\epsilon^{\frac{1}{2}}}}{|\Gamma[2+i(Z^*/\epsilon^{\frac{1}{2}})]|^2}|W|^2,\qquad l=1;\ m=-1,0,+1 \tag{20}$$

where

$$W=\int\!\!\int_\infty e^{-\{(1+\alpha)r_1+\alpha r_2\}}[3r_2\{1+\gamma(r_1-r_2)^2\}+\beta\hat{r}\{r_1(x^3/5-x)+r_2(x^2+3)\}]$$
$$\cdot\left[\int_{-i(\epsilon)^{\frac{1}{2}}}^{i(\epsilon)^{\frac{1}{2}}}e^{\zeta r_2}(\zeta+i(\epsilon)^{\frac{1}{2}})^{1+iZ^*/\epsilon^{\frac{1}{2}}}(\zeta-i(\epsilon)^{\frac{1}{2}})^{1-iZ^*/\epsilon^{\frac{1}{2}}}d\zeta\right]r_1^2dr_1r_2^3dr_2. \tag{21}$$

The integration of Eq. (21) is effected first by inverting the order of integration and then applying the theorem of residues for the evaluation of complex integrals. The process is essentially similar to that used by Fues[8] and Sugiura,[10] except that here we have to consider also the residue at infinity. Omitting all detailed steps, we write the final result as follows:

$$W=\frac{24^2\pi}{(1+\alpha)^3}\frac{Z^*(Z^{*2}+\epsilon)}{1-e^{2\pi Z^*/\epsilon^{\frac{1}{2}}}}\Bigg[\Bigg\{\frac{\beta(\alpha+Z^*)}{(1+\alpha)^4Z^*(Z^{*2}+\epsilon)}-\left(\frac{1}{3}+\frac{4\gamma}{(1+\alpha)^2}\right)\frac{(Z^*-2\alpha)}{(\alpha^2+\epsilon)^3}$$
$$+\frac{\{30\gamma-5\beta(1+\alpha)\}}{3(1+\alpha)(\alpha^2+\epsilon)^4}\left[\alpha^2+2Z^*\alpha+\frac{2}{5}(1-Z^{*2})\right]+\frac{30\gamma}{(\alpha^2+\epsilon)^5}\Bigg[\frac{2}{3}\alpha^3-Z^*\alpha^2+\frac{2}{5}(Z^{*2}-\epsilon)\alpha$$
$$+\frac{Z^*}{45}(7\epsilon-2Z^{*2})\Bigg]\Bigg]\Bigg\}\exp\left[-\frac{2Z^*}{\epsilon^{\frac{1}{2}}}\tan^{-1}\frac{\epsilon^{\frac{1}{2}}}{\alpha}\right]-\beta\Bigg\{\frac{\alpha+Z^*}{(1+\alpha)^4Z^*(Z^{*2}+\epsilon)}-\frac{2(2\alpha+3-Z^*)}{(1+\alpha)^3(Z^{*2}+\epsilon)}$$
$$+\frac{2}{(1+\alpha)^2\{(2\alpha+1)^2+\epsilon\}^2}+\frac{2(4\alpha+2-Z^*)}{3(1+\alpha)\{(2\alpha+1)^2+\epsilon\}^3}\Bigg\}\exp\left[-\frac{2Z^*}{\epsilon^{\frac{1}{2}}}\tan^{-1}\frac{\epsilon^{\frac{1}{2}}}{2\alpha+1}\right]\Bigg]. \tag{22}$$

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[10] Y. Sugiura, Scient. Pap. of Inst. of Phys. and Chem. Res. (Tokyo), No. 193 (1929).

IV. INTENSITY OF EMISSION, EFFECTIVE CROSS SECTION OF COMBINATION, AND THE ATOMIC COEFFICIENT OF ABSORPTION FOR H$^-$

(a) To calculate the total intensity of emission one must assume a definite distribution of electrons while they are mixed with the atoms. Since we are here dealing with neutral atoms only, we shall assume that their effect on the distribution of electrons can be neglected for the present purpose. This cloud of free electrons may be considered to behave exactly like an ideal gas in a fixed enclosure, having for the aggregate an electron temperature, T_e. Hence, we can apply the results of the quantum statistics for free electrons.

From the preceding section it can be shown[10] that $(a^2/Rh)\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}dE$ represents the amplitude squared of the matrix component for the transition of an electron having its energy lying between E and $E+dE$. Here a^2/Rh is the conversion factor from the units used in the preceding sections into c.g.s. units; $E=Rh\epsilon$. Therefore $(e^2a^2/Rh)\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}dE$ is to be interpreted as the square of the amplitude of electric moment. If g_E is the number of free electron states in the energy interval between E and $E+dE$, then $(e^2a^2/g_ERh)\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}dE$ is the weighted mean of the amplitude squared of the electric moment. We need only to multiply this by the total number of electrons in dE to obtain the total amplitude squared of the electric moment. By the well-known quantum statistics,[11] the total number of electrons in the energy interval between E and $E+dE$ is equal to $g_E\cdot\mathfrak{F}$ where $\mathfrak{F}$ is the average number of electrons per state. Therefore the total amplitude squared of the electric moment is

$$(e^2a^2\mathfrak{F}Rh)\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}dE. \tag{23}$$

Now the electric moment vibrates with a frequency ν determined by the equation

$$h\nu=E+e\Phi, \tag{24}$$

where Φ= electron affinity of the normal hydrogen atom. By referring to the classical electrodynamics for the radiation from a dipole oscillator, we can get the following wave-mechanical equivalent for the intensity of the continuous spectrum:

$$I(\nu)d\nu=N^0\cdot\frac{64\pi^4\nu^4e^2a^2}{3c^3Rh}\mathfrak{F}\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}dE, \tag{25}$$

where $hd\nu=dE$, by Eq. (24); $I(\nu)d\nu$= time rate of emission energy in ergs per sec. per cc in the frequency interval between ν and $\nu+d\nu$; N^0 = number of normal hydrogen atoms per cc. The $\mathfrak{F}$-function may be assumed to be that of an ideal electron gas obeying the new statistics of Fermi and Dirac, namely

$$\mathfrak{F}=1/ce^{E/kT_e}-1, \tag{26}$$

where T_e= electron temperature, and C= function of T_e and electron density. Fermi[12] showed that for very large T_e,* C is so large that $Ce^{E/kT}\gg 1$. Hence we have the Maxwell's distribution and the $\mathfrak{F}$-function is accordingly

$$\mathfrak{F}=[N^eh^3/(2\pi mkT_e)^{\frac{3}{2}}]e^{-E/kT_e}, \tag{26a}$$

where N^e is the number of electrons per cc. Combining Eqs. (25) and (26a), we have

$$\frac{I(\nu)}{N^0N^e}=\frac{64\pi^4\nu^4e^2a^2}{3c^3R}\cdot\frac{h^3}{(2\pi mkT_e)^{\frac{3}{2}}}e^{-E/kT_e}\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}. \tag{27}$$

(b) The effective cross section of combination for an atom (q) may be defined as the cross section of a small sphere such that the number of electrons with velocity v striking the surface of the sphere will be equal to the number of electrons with the same velocity actually captured by the atom. If $n(E)dE$ is the number of electrons per cc in the energy interval between E and $E+dE$ (according to Maxwell's distribution), then

$$n(E)dE=[2\pi N^eE^{\frac{1}{2}}/(\pi kT_e)^{\frac{3}{2}}]e^{-E/kT_e}dE, \tag{28a}$$

$$I(\nu)d\nu=N^0h\nu\cdot qvn(E)dE. \tag{28b}$$

Solving for q, we get

$$q=[16\pi^3h\nu^3/3(mv)^2c^3]e^2a^2\sum_{l,\,m}M^2_{\epsilon,\,l,\,m}. \tag{29}$$

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[11] E.g., G. Birtwistle, *The New Quantum Mechanics*, Chap. XXIX. E. Fermi, Zeits. f. Physik **36**, 902 (1926).

[12] E. Fermi, Zeits. f. Physik **36**, 902 (1926).

* We are here interested only in large T_e. (See Section V.)

(c) The atomic coefficient of absorption (k) for H^- may be similarly defined as the effective cross section of H^- for the capture of quanta of radiation. The number of quanta captured, or the number of H^- atoms dissociated, per second per cc in the frequency interval between ν and $\nu+d\nu$ is clearly

$$kc\rho d\nu/h\nu$$

where $\rho d\nu$= radiation energy density in the same frequency interval.

Assuming thermal equilibrium between emission and absorption processes (extension of Einstein's method to transitions between continuous and discrete states), Kramers[13] and Milne[14] derived the following relation between q and k

$$q/k=2gh^2\nu^2/m^2v^2c^2, \qquad (30)$$

where g is the statistical weight of the lower energy state in this case, $g(H^-)=1$. The explicit expression for k in terms of the square of the matrix component of transition is

$$k=(8\pi^3\nu/3cRh)e^2a^2\sum_{l,m}M^2_{\epsilon,l,m}. \qquad (31)$$

V. Numerical Computations

The three constants in the H^- wave function given by Hylleraas are in the units here used: $\alpha=0.770$, $\beta=0.308$, and $\gamma=0.119$. To fit the expression in Eq. (9) with that in Eq. (8) for large values of the radial variable, Z^* may take any value ranging between 0 and 0.5, depending upon which portion of the curve is to be fitted best. Various values of Z^* in this range have been tried in the present calculation. Except for slight differences in numerical magnitudes, they give approximately the same distribution of $\sum_{l,m}M^2_{\epsilon,l,m}$ as a function of the energy parameter ϵ. For illustration, we have chosen for Z^* a value of 0.42, although much smaller values will equally serve the purpose. The values for $\sum_{l,m}M^2_{\epsilon,l,m}$ are not critical to the variation of Z^*, so that the general interpretation of results about to be obtained will not necessarily depend upon any particular value of Z^*.

The electron affinity of the normal hydrogen atom is given by Hylleraas as 0.715 v, with which we can calculate the frequency of radiation for any kinetic energy of the electron (by Eq. (24)).

Now, we will consider the order of magnitude of the electron temperature (T_e). Langmuir and Mott-Smith[15] find a temperature of about 30,000°C at 2×10^{-4} mm pressure in discharges through mercury vapor. Kopfermann and Ladenburg[16] find convincing evidence for statistical equilibrium in discharges through neon at 1 mm pressure with an electron temperature of about 22,000°C. From these evidences and others, it seems certain that the electron temperature under electrical discharge conditions must be

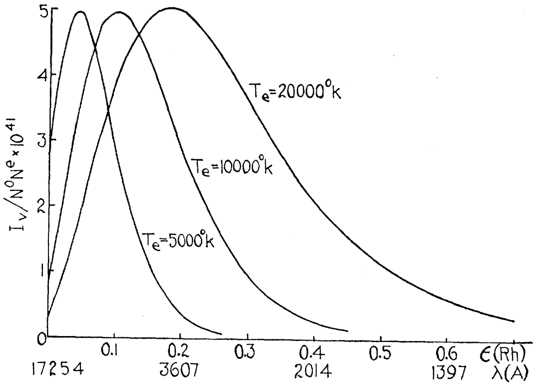

FIG. 1. Intensity distribution at different electron temperatures.

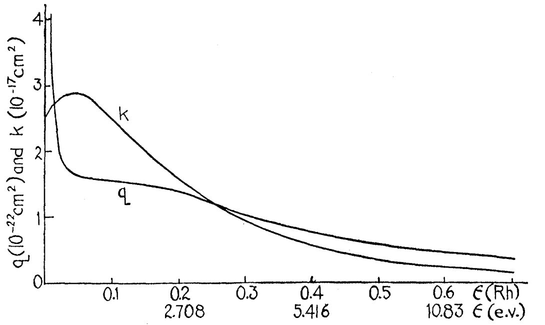

FIG. 2. Effective cross section of combination (q) and coefficient of absorption for H^- (k).

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[13] H. A. Kramers, Phil. Mag. **46**, 836 (1923).

[14] E. A. Milne, Phil. Mag. **47**, 209 (1924).

[15] J. Langmuir and H. Mott-Smith, Gen. Elec. Rev. **27**, 449 (1924).

[16] H. Kopfermann and R. Ladenburg, Naturwiss. **5**, 513 (1931).

quite high. In the present calculations of the emission spectrum we shall choose several different values of electron temperature to illustrate its effect upon the general distribution of emission intensities.

The accompanying graphs (Figs. 1 and 2) show the results of computation for the emission intensities at different electron temperatures, the effective cross section of combination, and the coefficient of absorption for H^-.

CONCLUSION

(a) Discussion of results

The computed results show that the intensity per unit frequency interval in the emission spectrum has a low but finite value at the long wave limit. There is a point toward the short wave side of the limit where the intensity has its maximum value, which is displaced more and more away from the limit as the electron temperature is raised. Thus, at a very high electron temperature (e.g., 20,000°K) the intensity at the limit may be more than ten times smaller than the maximum value whose spectral position is considerably away from the limit (see Fig. 1). If the absolute magnitude of the intensity is low, then the limit would be so faint that it is beyond recognition. The identification of the continuous spectrum and the subsequent determination of electron affinity by the position of the limit would become very difficult.

The curve for the effective cross section of combination (see Fig. 2) is similar in appearance to that of the recombination between H^+ and electrons obtained by Stueckelberg and Morse,[17] except that the order of magnitude of the former is much smaller and it does not diminish as rapidly for high-velocity electrons. It must be mentioned here that the present calculations are based on random distribution of electrons while Stueckelberg and Morse assumed a unidirectional stream of electrons. For a more exact comparison, we have calculated the effective cross section in exact accordance with Stueckelberg and Morse's method. The resulting value is not shown in the figure, but is about 100–500 times smaller than for their case. If the concentration of the corresponding reaction quantities (i.e., the number of H^- atoms and electrons in one case and the number of H^+ atoms and electrons in the other) are the same, the emission intensities would bear the same ratio. Hence the intensity of the electron affinity spectrum for normal hydrogen atoms is expected to be generally very low.

The curve for the atomic coefficient of absorption (see Fig. 2) has a maximum near the limit of the continuous absorption spectrum. The magnitude of the coefficient is generally higher than the values for caesium given by Mohler[18] (possibly by as much as 100-fold). If there is sufficient concentration of H^- ions present, it should be possible (apart from the experimental difficulties) to obtain a continuous absorption spectrum due to the photo-ionization of H^- ions.

(b) Application of the results to the electron affinity spectrum of halogen atoms

The halogen atoms are known to have great affinity for electrons and their negative ions have a stable external configuration similar to the inert gases. If the negative ions are formed by an elementary process of combination between neutral atoms and electrons, the emission spectrum of halogen atoms should be very roughly similar to that of hydrogen. On this qualitative basis we expect that the conclusions obtained for hydrogen may partially apply to the continuous spectrum of halogen atoms.

In his recent experiments, Oldenberg found no trace of an electron affinity spectrum for the iodine atom under widely varying experimental conditions. The possibility of having a distribution of intensities such that the maximum intensity is far separated from the spectral limit becomes less for the iodine atom because of the slower change of the ν^4-factor at a larger electron affinity (about 3.2 volts). It seems that the only other alternative is to assume that the intensity of emission is too faint to be experimentally detectable; or in other words, the combination between neutral iodine atoms and electrons with simultaneous emission of radiation is comparatively an improbable process—a conclusion reached by Oldenberg.

Strictly speaking, however, we are not justified to make quantitative comparisons between the

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[17] E. C. G. Stueckelberg and P. M. Morse, Phys. Rev. **36**, 16 (1930).

[18] F. L. Mohler, Phys. Rev. Sup. **1**, 2 (1929).

two cases for at least two reasons. First, the present calculations for hydrogen are based upon very rough wave functions in the continuous state; hence the solution is far from being rigorous and exact. The results may be expected, at best, to be only approximately correct for hydrogen and must not be applied directly to the halogen atoms, which presumably have quite different potential functions. Secondly, the difference in magnitudes of electron affinity between the halogen atoms and hydrogen is quite large—the halogen atoms have electron affinities in the range of 3–4 volts against about 0.7 v for hydrogen. The influence of the magnitude of electron affinity comes in when one deals with the ν^4-factor in the expression for intensity. Under these circumstances we cannot expect to have a simple quantitative relation between the two problems.

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