

## ON THE PHOTO-IONIZATION OF MOLECULES.

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### I. INTRODUCTION

The subject of photo-ionization of molecules has hitherto received scant attention both from experimenters and theoretical physicists. The importance of the subject was first pointed out by Prof. M. N. Saha (1935), who suggested that the electrons in the ionosphere may, in part, be due to the ionization of  $N_2$  to  $N_2^+$  and  $O_2$  to  $O_2^+$ , each in two different ways. The present attempt dealing theoretically with the photo-ionization of  $H_2$  to  $H_2^+$  was made at the suggestion of Prof. Saha, as it was felt that the cases of  $N_2$  and  $O_2$  are rather too complex and a start might be made with the  $H_2$ -molecule in this direction, on account of simplicity of structure of the latter.

We have not been able to trace any previous theoretical attempt on this problem. Regarding the experimental work, the following report in *Die Physik* by Joos and Finkelnburg (1935) and Prof. Saha's remarks on the same may prove interesting :

'Ionization continua of molecules have not been demonstrated so far, and the only attempt hitherto known to explain absorption continua of a polyatomic molecule was by Henning (*Ann. der Physik.*, 13, 599, 1544) and the ionization spectrum is not at all convincing. Since the ionization continua must naturally be possible also in the case of molecules, it remains to be investigated why photo-ionization of molecules is apparently such an improbable process. The scheme of molecular potential curves of which we shall speak later (Section on molecular continuum), and the Frank-Condon Principle which controls transitions between molecular states appear to offer a possibility for its explanation. In the term-scheme, it is usually found that the continuous eigen-spectrum corresponding to ionization are usually superposed on the continuous eigen-value region of different excited states which lead to dissociation. According to Frank-Condon Principle, the transitions from the ground state are very probable, and if we consider the part of the transition-probability due to the electron it is apparently more probable than transitions to the continuous eigen-value spectrum corresponding to ionization. The following observations seem to hold generally:—

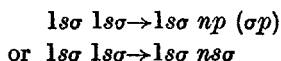
The ionization of a molecule by light-quanta appear to be less probable than dissociation of the molecule by absorption of the same light-quanta into

a normal and an excited atom with a certain amount of kinetic energy. In this way, we can understand why extended intensive dissociation continua of molecules have been obtained, while molecular photo-ionization has not been shown.'

With respect to the above remarks Dr. Saha has been kind enough to communicate to us the following:—

'While agreeing mostly with these remarks, it may be pointed out that Joos and Finkelburg have probably omitted to mention one significant cause of the absence of any experimental proof of molecular photo-ionization. In the case of most of the ordinary gases, this lies in a region where absorption experiments are extremely difficult, and have not therefore been properly carried out. For example, for  $H_2$  it begins at  $\lambda$  840, for  $O_2$  at  $\lambda$  1019 (feeble) and at  $\lambda$  747 (strong), for  $N_2$  at  $\lambda$  794 (feeble) and at  $\lambda$  660 (strong). The same remark may be made with respect to other gases. The other cause mentioned by Joos and Finkelburg is of course effective, but the proportion of photons which cause dissociation may be widely different for different gases and needs investigation.'

Let us see how previous workers are correct in their assumptions on the variation of photo-ionization with frequency. Let us denote the absorption coefficient by  $\tau(\nu)$  and the frequency by  $\nu$ . Pannekoek (1926) and Chapman (1931) assumed that the  $\tau(\nu)/\nu$ -curve for molecular photo-ionization is of the same nature as the atomic photo-ionization curve, *i.e.*  $\tau(\nu)$  begins with a maximum value at the threshold value of  $\nu = \nu_0$ ,  $h\nu_0 = eV_1$  where  $V_1$  = the ionization potential, but diminishes with increasing  $\nu$  as  $1/\nu^3$  roughly. It is evident that this assumption is incorrect for molecular photo-ionization; for, the case of molecules is complicated by the fact that the nuclear distance changes in course of ionization. We illustrate by taking the case of the  $H_2$ -molecule. The process of ionization of  $H_2$  may be illustrated symbolically as



*i.e.* one electron goes to infinity by having its  $l$ -quantum changing from  $0(1s)$  to  $l(mp)$  and the total quantum number  $n \rightarrow \infty$ . But the nuclear distance in normal  $H_2$  is  $0.749 \times 10^{-8}$  cms. while in normal  $H_2^+$  it is  $1.070 \times 10^{-8}$  cms. According to the Frank-Condon Principle, during an electron-transition, the nuclear distance remains unchanged; when applied to the present case, this means that  $H_2^+$  -ion will be left in a vibrational state, with a large value of  $V$ , the vibrational quantum number. Hence the strongest transition will be from  $V'' = 0$  to  $V' =$  some integral number, but the transition  $V'' = 0$  to  $V' = 0$  is expected to be rather feeble, as the nuclear distance in  $H_2^+$  for  $V' = 0$ , *viz.*, the  $1.070 \times 10^{-8}$  cm. is very different from the nuclear distance in  $H_2$ , *viz.*,  $0.709 \times 10^{-8}$  cm. Hence, the lowest frequency  $\nu = \nu_0 + \frac{1}{2}\omega_0'$  ( $\nu_0$  being the electronic transition frequency,  $\omega_0'$  = normal frequency of nuclear vibration of

$\text{H}_2^+$ ) will be rather very feebly absorbed. The strongest absorption will take place at the frequency  $\nu = \nu_0 + (V' + \frac{1}{2}) \omega_0'$  where  $V'$  is the particular quantum number for that vibration of  $\text{H}_2^+$  when the least distance between the nuclei of  $\text{H}_2^+$  is  $0.709 \times 10^{-8}$  cm.

The investigations which are reported below have confirmed these expectations.

## 2. CALCULATION OF PHOTO-IONIZATION

Let  $I_{0\nu}$  be the intensity of a beam of light of frequency  $\nu$  initially, and  $I_{l\nu}$  the intensity after the beam has passed through a length  $l$  cms. of a gas at N.T.P. Then we have

$$I_{l\nu} = I_{0\nu} \exp(-\alpha_\nu l) = I_{0\nu} \exp(\tau(\nu)Nl) \quad \dots \quad (1)$$

where  $\tau(\nu)$  is absorption per molecule,  $N$  the number of molecules per c.c. Then the absorption coefficient  $\tau(\nu)$  as given by Bethe (1933) is given by

$$\tau(\nu) d\nu = \frac{8\pi^3\nu}{hc} \left| M_{kk'} \right|^2 dE \quad \dots \quad (2)$$

where  $|M_{kk'}|$  denotes the transition probability from a state  $k$  to  $k'$  associated with the absorption of a photon  $h\nu$ , and  $dE$ , the range in energy. In the present case, we should remember that the transition is from a 'bound' state of the electron in the hydrogen molecule to a 'free' state of the electron in the ionized hydrogen molecule. The matrix component in Eq. (2) is defined by the equation

$$|M_{kk'}| = \int \psi_k [M] \psi_{k'} d\Omega \quad \dots \quad (3)$$

where  $\psi_k$  is the wave function of the initial state (of the  $\text{H}_2$  molecule),  $\psi_{k'}$  that of the final state (of the molecule with the 'free' electron in a continuous energy state),  $[M]$  is the electric moment (a function of all the co-ordinates involved), and the integration extends throughout the entire space whose element is  $d\Omega$ .

The assumption we have to make in our case is, as proposed by Born and Oppenheimer (1927) and followed by Hutchisson (1930), that the eigenfunctions  $\psi_k(\text{H}_2)$ ,  $\psi_{k'}(\text{H}_2^+ : e)$  are products of electronic, vibrational and rotational eigen-functions; further, let us assume that the functions  $\psi_k(\text{H}_2)$  and  $\psi_{k'}(\text{H}_2^+ : e)$  are normalized, and the nuclear distance is regarded as a constant parameter while the integration is carried out over the electronic co-ordinates.

We proceed according to Condon (1928) and Hutchisson (1930), and split up the electric moment  $[M]$  into sum of two moments, *i.e.*  $[M] = M_e(r) + M_v(q)$  where  $M_e(r)$  is the electric moment associated with the electronic transition and  $M_v(q)$  that associated with the vibrational transition corresponding to a change in the internuclear distance  $q$ . Next, let us split up the eigen-functions  $\psi(\text{H}_2)$  and  $\psi(\text{H}_2^+ : e)$  into  $\psi_1(e)\psi_1(v)\psi_1(m)$  and  $\psi_2(e)\psi_2(v)\psi_2(m)$ , where  $e$ ,  $v$ ,  $m$  respectively stand for electronic, vibrational and rotational

motions. The suffixes 1 and 2 in the eigen-functions refer respectively to the initial ( $H_2$ ) and final ( $H_2^+ : e$ ) states. Thus  $\psi_1(m)$  denotes the eigen-function for rotation only in the initial state, and  $\psi_2(m)$  the same in the final state. Similar interpretations are implied for the functions  $\psi_1(v), \psi_2(v)$  and  $\psi_1(e), \psi_2(e)$ . One must guard against the confusion that  $\psi_1(m), \psi_1(v), \psi_1(e)$  are the same functions of  $m, v, e$  anymore than  $\psi_2(m), \psi_2(v), \psi_2(e)$  are the same functions of  $m, v, e$  respectively. To avoid cumbersome notations with regard to the above functions, we have used these simplifications, whose import is quite evident.

Splitting up the eigen-functions of  $\psi(H_2)$  and  $\psi(H_2^+ : e)$  into  $\psi_1(e)\psi_1(v)\psi_1(m)$  and  $\psi_2(e)\psi_2(v)\psi_2(m)$  respectively, we get

$$|M_{kk'}| = \iiint \psi_1(e)\psi_1(v)\psi_1(m)[M]\psi_2(e)\psi_2(v)\psi_2(m)d\Omega \\ = \int \psi_1(m)\psi_2(m)d\phi \int \int \psi_1(e)\psi_1(v)[M_e(r) + M_v(g)]\psi_2(e)\psi_2(v)d\Omega_e d\Omega_v \dots (4)$$

where  $\int \dots d\Omega_e, \int \dots d\Omega_v$  denote integration with respect to electron co-ordinates and nuclear co-ordinates respectively. The above can be further split up into principal parts. Thus

$$|M_{kk'}| = \int \psi_1(m)\psi_2(m)d\phi \left[ \int \psi_1(e)\psi_2(e)d\Omega_e \int \psi_1(v)M_v(g)\psi_2(v)d\Omega_v \right. \\ \left. + \int \psi_1(v)\psi_2(v)d\Omega_v \int \psi_1(e)M_e(r)\psi_2(e)d\Omega_e \right] \dots (5)$$

The  $H_2^+$  -ion together with the electron in the continuous energy state can be regarded as an excited state of the normal  $H_2$ -molecule. This means that  $\psi_1(e)$  and  $\psi_2(e)$  are orthogonal to each other, and consequently the contribution of the first part to  $|M_{kk'}|$  is nil. The contribution due to the second part cannot be zero, in general, as the vibrational states do not refer to the same molecule, *i.e.*  $\int \psi_1(v)\psi_2(v)d\Omega_v \neq 0$ . The transition probability thus reduces to

$$|M_{kk'}| = \int \psi_1(m)\psi_2(m)d\phi \int \psi_1(v)\psi_2(v)d\Omega_v \int \psi_1(e)M_e(r)\psi_2(e)d\Omega_e \dots (6)$$

The first factor of  $|M_{kk'}|$  *viz.*,  $\int \psi_1(m)\psi_2(m)d\phi$  involves the rotational states, and, at any rate, contributes a constant which may be taken to be unity, whatever be the nature of transitions (vide Condon, *Phys. Rev.*, Vol. 32, p. 858, 1928, line 9); we may leave this part out of account for our future treatment. The second factor, *viz.*,  $\int \psi_1(v)\psi_2(v)d\Omega_v$  concerns nuclear oscillation. This is taken up subsequently. We consider now the third factor, *viz.*,  $\int \psi_1(e)M_e(r)\psi_2(e)d\Omega_e$ . Here  $\psi_1(e)$  denotes the lowest state of the  $H_2$ -molecule which can be regarded as being made up of two H-atoms in the  $1s$  states. We have therefore

$$\psi_1(e) = \frac{1}{\sqrt{2 \pm S}} \left[ u(a1)_{1s} u(b2)_{1s} \pm u(a2)_{1s} u(b1)_{1s} \right] \dots (7)$$

where  $u(a1)_{1s}$  is the normalized wave-function of the H-atom with electron (1) in the  $1s$ -state with respect to nucleus ( $a$ ). Similarly for the other  $u$ 's.

In Hartree units we have (vide Bethe, *Handbuch der Physik*, 24, p. 284, Eq. (3. 18), 1934):

$$\left. \begin{aligned} u(a1)_{1s} &= 2 \exp(-r_{a1}); & u(a2)_{1s} &= 2 \exp(-r_{a2}); \\ u(b1)_{1s} &= 2 \exp(-r_{b1}); & u(b2)_{1s} &= 2 \exp(-r_{b2}); \end{aligned} \right\} \dots \quad (8)$$

and

$$\begin{aligned} S^2 &= \iint u(a1)_{1s} u(b1)_{1s} u(a2)_{1s} u(b2)_{1s} d\Omega_1 d\Omega_2 \\ &= \left[ \int u(a1)_{1s} u(b1)_{1s} \right]^2 \dots \dots \dots \dots \dots \quad (9) \end{aligned}$$

The integral  $S$  was originally introduced by Suguira (1927) and has the value  $(1+q+q^2/3) \exp(-q)$  in Hartree units,  $q$  = nuclear distance in the same units. As is well known  $\psi_1(e)$ , as expressed by (7), is only an approximate form and represents the zeroeth order of approximation.

As regards  $\psi_2(e)$ , the wave function of  $H_2^+$  and the free electron, we can follow the method of Heitler and London (1927), by replacing one of the eigenfunctions by a continuous eigen-function denoting  $\infty S$ -state. Further improvements on the Heitler-London model of  $H_2$  have been worked out by Wang (1928), Hylleraas (1931) and others, but for the present we stick to the HL-model.

Let  $u(a1)_{cs}$  represent the normalized wave function for the continuous state of the H-atom, the electron 1 being in a continuous positive energy state with respect to the nucleus 'a' and let 'cs' denote that the electron is in the continuous energy state with  $l = 0$ . The energy of the free electron may be anything from 0 to  $\infty$ . Similarly, the continuous state may be a  $p$ - or a  $d$ -state represented by  $u(a1)_{cp}$  or  $u(a1)_{cd}$  and so on. Following Kemble and Zener (1929), we may consider the wave-functions of the excited states of  $H_2^+$ -molecule as built up of an excited H-atom and a normal H-atom, the electron in the excited H-atom being in the  $\infty s$  or  $\infty p$  states. The  $\infty p$  state again gives 3  $\psi$ -functions according as the  $m$ -quantum number is 1, 0, or  $-1$ . Thus there will be four  $\psi$ -functions representing the  $H_2^+$ -molecule which consist of the first electron in the  $1s$ -state with respect to the nucleus 'a', and the second electron in  $\infty s$  or  $\infty p(1, 0, -1)$  state with regard to nucleus 'b'. If we exchange nuclei, or electrons, or both, we get three more sets of wave-functions. Each set consists of 4 wave-functions denoting the  $\infty s$  and  $\infty p(1, 0, -1)$  states. These are Kemble and Zener's 16 wave-functions. Exactly similar expressions may be obtained for the electrons in the continuous state, which may be  $\infty d$  or  $\infty f$  states, etc., giving an infinite number of wave-functions.

At the outset, however, we shall confine our attention, for the sake of simplicity of treatment, to the simplest transition, *viz.*, from  $1s^2$  to  $(1s\infty s)$  state. This gives us only the  ${}^1\Sigma_u$ -state, but other  ${}^1\Sigma$ -states with the same energy-value will arise, from combination  $1s\infty p\sigma$ ,  $1s\infty d\sigma$ , but these are not considered here. We obtain, in that case, four wave-functions by interchange of nuclear and electronic co-ordinates. These are

$$\left. \begin{aligned} \psi(1) &= u(a1)_{1s} u(b2)_{cs}; & \psi(2) &= u(a2)_{1s} u(b1)_{cs}; \\ \psi(3) &= u(a2)_{cs} u(b1)_{1s}; & \psi(4) &= u(a1)_{cs} u(b2)_{1s}; \end{aligned} \right\} \dots \quad (10)$$

where

$$u(a1)_{cs} = -\frac{\sqrt{2}}{\sqrt{1-\exp(-2\pi n')}} \cdot \frac{1}{2kr_{a1}} \times \frac{1}{2\pi} \oint_{\xi} (\xi + \frac{1}{2})^{-in'-1} (\xi - \frac{1}{2})^{in'-1} \exp(-2ikr_{a1}\xi) d\xi \dots \quad (11)$$

and the contour is taken along a path enclosing the two branch-points at  $\xi = \pm \frac{1}{2}$ . For the above expression see Bethe, *loc. cit.*, p. 293, formula (4.22). In this latter formula put  $l = 0$  and we get to the result (11). This method of writing out the eigen-function of  $(H_2^+, \text{ and } e)$  is of course approximate, as in the original treatment of  $H_2$  by Heitler and London, but further improvements may be taken up later on.

We observe that  $\psi(3)$  is obtained from  $\psi(1)$ , by interchange of 'a' and 'b';  $\psi(4)$  from  $\psi(2)$ , by interchange of 'a' and 'b';  $\psi(2)$  from  $\psi(1)$ , by interchange of 1 and 2;  $\psi(4)$  from  $\psi(3)$ , by interchange of 1 and 2.

Using the symbols  $S^E, A^E, S^N, A^N$  to denote symmetry in the wave-functions for an interchange of electronic and nuclear co-ordinates, or anti-symmetry for the same, we form the wave-functions of the H-ion, as a linear combination of  $\psi(1), \psi(2), \psi(3), \psi(4)$  and indicate its symmetry or anti-symmetry in the electrons or nuclei. Thus

$$\psi(H_2^+ : e) \left. \begin{aligned} \phi_1 &= C_1[\psi(1) + \psi(2) + \psi(3) + \psi(4)]; & (S^E S^N) \\ \phi_2 &= C_2[\psi(1) + \psi(2) - \psi(3) - \psi(4)]; & (S^E A^N) \\ \phi_3 &= C_3[\psi(1) - \psi(2) + \psi(3) - \psi(4)]; & (A^E S^N) \\ \phi_4 &= C_4[\psi(1) - \psi(2) - \psi(3) + \psi(4)]; & (A^E A^N) \end{aligned} \right\} \dots \quad (12)$$

For normalization we notice that we should have

$$\int \phi_1^2 d\Omega = \int \phi_2^2 d\Omega = \int \phi_3^2 d\Omega = \int \phi_4^2 d\Omega = 1. \dots \quad (13)$$

Let us define the following integrals:

$$\left. \begin{aligned} A &= \int \psi(1)\psi(2)d\Omega = \int u(a1)_{1s}u(b1)_{cs}d\Omega_1 \int u(a2)_{1s}u(b2)_{cs}d\Omega_2 = X^2; \\ B &= \int \psi(1)\psi(3)d\Omega = \int u(a1)_{1s}u(b1)_{1s}d\Omega_1 \int u(a2)_{cs}u(b2)_{cs}d\Omega_2 = SY; \\ C &= \int \psi(1)\psi(4)d\Omega = \int u(a1)_{1s}u(a1)_{cs}d\Omega_1 \int u(b2)_{1s}u(b2)_{cs}d\Omega_2 = 0; \\ D &= \int \psi(2)\psi(3)d\Omega = \int u(b1)_{1s}u(b1)_{cs}d\Omega_1 \int u(a2)_{1s}u(a2)_{cs}d\Omega_2 = 0; \\ E &= \int \psi(2)\psi(4)d\Omega = \int u(a1)_{cs}u(b1)_{cs}d\Omega_1 \int u(a2)_{1s}u(b2)_{1s}d\Omega_2 = SY; \\ F &= \int \psi(3)\psi(4)d\Omega = \int u(b1)_{1s}u(a1)_{cs}d\Omega_1 \int u(b2)_{1s}u(a2)_{cs}d\Omega_2 = X^2. \end{aligned} \right\} \quad (14)$$

We notice that F is obtained from A by interchange of nuclei, E from B by interchange of electrons, and C from D by interchange of both nuclei and electrons. Further, we have  $A = F = X^2$  where  $X$  is the integral  $\int u(a1)_{1s}u(b1)_{1s}d\Omega_1$ . Similarly, we have  $B = E = SY$  where  $S = \int u(a1)_{1s}u(b1)_{1s}d\Omega_1$  and is the 'Sugura Integral', already referred to. The integral  $Y = \int u(a2)_{cs}u(b2)_{cs}d\Omega_2$  is entirely of a new type. We observe, further, that integrals C and D are each equal to zero, from conditions of orthogonality. We therefore have

$$\left. \begin{aligned} \iint \psi(1)\psi(2)d\Omega_1d\Omega_2 &= \iint \psi(3)\psi(4)d\Omega_1d\Omega_2 = X^2, \\ \iint \psi(1)\psi(3)d\Omega_1d\Omega_2 &= \iint \psi(2)\psi(4)d\Omega_1d\Omega_2 = SY. \end{aligned} \right\} \dots (15)$$

Now the conditions deduced give us for the normalizing factors:

$$\left. \begin{aligned} C_1 &= \frac{1}{2\sqrt{1+X^2+SY}}, & C_2 &= \frac{1}{2\sqrt{1+X^2-SY}}, \\ C_3 &= \frac{1}{2\sqrt{1-X^2+SY}}, & C_4 &= \frac{1}{2\sqrt{1-S^2-SY}}. \end{aligned} \right\} \dots (16)$$

### 3. CALCULATION OF ELECTRONIC TRANSITION PROBABILITY

We have already stated that the nuclear distance is to be regarded as constant during electronic transition; but due to the vibrational transitions which accompany the electronic transitions this distance may change considerably. The electric moment corresponding to electronic transition is given by

$$e \left( \overset{\rightarrow}{r}_{a1} + \overset{\rightarrow}{r}_{b1} + \overset{\rightarrow}{r}_{a2} + \overset{\rightarrow}{r}_{b2} \right) \dots \dots \dots (17)$$

where  $\overset{\rightarrow}{r}_{a1}$  etc. denote vectors and the summation is vectorial. Choosing the component of the electric moment along the internuclear axis, *i.e.*, our  $z$ -axis, we have

$$M_z(z) = e(r_{a1} \cos \theta_1 + r_{b1} \cos \phi_1 + r_{a2} \cos \theta_2 + r_{b2} \cos \phi_2) \dots (18)$$

where  $\theta_1, \theta_2, \phi_1, \phi_2$  are the angles shown in Fig. 1. We need not calculate

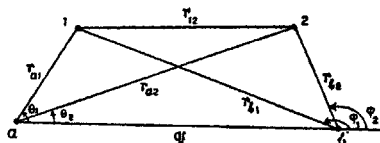


FIG 1.

the  $M(x+iy)$  terms since they vanish due to the  $\phi$ -part of the integral. The component perpendicular to the nuclear axis  $= e(\rho_1 e^{i\phi_1} + \rho_2 e^{i\phi_2})$ , where  $\rho_1, \rho_2$  are the distances of electrons 1 and 2 from the internuclear axis, and  $\phi_1, \phi_2$

the angles between the planes (1 *a b*), (2 *a b*) and a fixed plane in space passing through the internuclear axis.

$$\therefore M_e(x+iy) = \frac{CC'}{q} \int [(\psi_1' + \psi_2') [\rho_1 e^{i\phi_1} + \rho_2 e^{i\phi_2}] (\psi(1) + \psi(2) + \psi(3) + \psi(4))] d\Omega$$

for the transition  $\psi(H_2): (S^E \cdot S^N) \rightarrow \psi(H_2^+ : e) : (S^E \cdot S^N)$ . [Cf. Eqns. 21-24 below.]

Since  $\rho_1, \rho_2$  are expressible in terms of  $q, r_{a1}, r_{b1}$ , etc. from elementary trigonometry and the  $\psi$ 's are functions of  $r_{a1}, r_{b1}$ , etc. only, the above can be split up into sum of two integrals  $M_e^1(x+iy)$  and  $M_e^2(x+iy)$  containing  $e^{i\phi_1} d\phi_1, e^{i\phi_2} d\phi_2$  as factors respectively in the integrands. Since the limits of these  $\phi$ 's are 0 and  $2\pi$  for either of the electron-spaces, both  $M_e^1$  and  $M_e^2$  vanish on account of this zero factor. Now we have

$$\left. \begin{aligned} r_{a1} \cos \theta_1 + r_{b1} \cos \phi_1 &= (r_{a1}^2 - r_{b1}^2)/q = z_1 \\ r_{a2} \cos \theta_2 + r_{b2} \cos \phi_2 &= (r_{a2}^2 - r_{b2}^2)/q = z_2 \end{aligned} \right\} \quad \dots \quad (19)$$

So we derive:

$$M_e(z) = M_e(z_1) + M_e(z_2) \quad \dots \quad (20)$$

where

$$\left. \begin{aligned} M_e(z_1) &= \frac{e}{q} (r_{a1}^2 - r_{b1}^2) \\ M_e(z_2) &= \frac{e}{q} (r_{a2}^2 - r_{b2}^2) \end{aligned} \right\}$$

We have further

$$\psi(H_2) = C(\psi_1' + \psi_2') \text{ or } C'(\psi_1' - \psi_2') \quad \dots \quad (21)$$

where

$$\left. \begin{aligned} \psi_1' &= u(a1)_{1s} u(b2)_{1s} \\ \psi_2' &= u(a2)_{1s} u(b1)_{1s} \end{aligned} \right\} \quad \dots \quad (22)$$

and

$$C = \frac{1}{\sqrt{2+2S^2}}, \quad C' = \frac{1}{\sqrt{2-2S^2}}. \quad \dots \quad (23)$$

We now try to find out the  $M_e(z)$ -value for the transition:

$$\psi(H_2)(S^E S^N) \rightarrow \psi(H_2^+ : e)(S^E S^N)$$

We have

$$M_e(z) = \frac{CC'}{q} \int [(\psi_1' + \psi_2') \{ (r_{a1}^2 - r_{b1}^2) + (r_{a2}^2 - r_{b2}^2) \} \times \{ \psi(1) + \psi(2) + \psi(3) + \psi(4) \}] d\Omega. \quad \dots \quad (24)$$

In order to evaluate this integral, we have to deal with 32 terms. Let us first consider the product of the  $\psi$ 's which are eight in number. These are



$$\left. \begin{aligned}
 A' &= \psi_1' \psi(1) = u(a1)_{1s} u(a1)_{1s} u(b2)_{1s} u(b2)_{cs}; \\
 B' &= \psi_1' \psi(2) = u(a1)_{1s} u(b1)_{cs} u(a2)_{1s} u(b2)_{1s}; \\
 C' &= \psi_1' \psi(3) = u(a1)_{1s} u(b1)_{1s} u(b2)_{1s} u(a2)_{cs}; \\
 D' &= \psi_1' \psi(4) = u(a1)_{1s} u(a1)_{cs} u(a2)_{1s} u(b2)_{1s}; \\
 E' &= \psi_2' \psi(1) = u(a1)_{1s} u(b1)_{1s} u(a2)_{1s} u(b2)_{cs}; \\
 F' &= \psi_2' \psi(2) = u(b1)_{1s} u(b1)_{cs} u(a2)_{1s} u(a2)_{1s}; \\
 G' &= \psi_2' \psi(3) = u(b1)_{1s} u(b1)_{1s} u(a2)_{1s} u(a2)_{cs}; \\
 H' &= \psi_2' \psi(4) = u(b1)_{1s} u(a1)_{cs} u(a2)_{1s} u(b2)_{1s}.
 \end{aligned} \right\} \dots \dots (25)$$

We observe the following symmetry relations amongst their products. By interchange of the nuclei 'a' and 'b', we pass from A to G, B to H, C to E and D to F. By interchange of electrons 1 and 2 we pass from A to F, B to E, C to H, and D to G.

It is found after some work (Note 1, p. 103) that the integrals contained in (24) either vanish, or all reduce to a single integral, viz.,

$$I = S \int u(a1)_{1s} u(b1)_{cs} (r_{a1}^2 - r_{b1}^2) d\Omega_1 \dots \dots (26)$$

One can evaluate this integral by the use of elliptic co-ordinates. It has been shown (in Note 1) that

$$I = \text{constant} \times$$

$$\oint_{\xi=1}^{\infty} \int_{\mu=1}^1 \exp\left(-\frac{\lambda q}{2} (1+2ik\xi)\right) \exp\left(-\frac{\mu q}{2} (1-2ik\xi)\right) (\lambda+\mu) F(\xi) d\mu d\lambda d\xi$$

where  $F(\xi) = (\xi + \frac{1}{2})^{-n'-1} (\xi - \frac{1}{2})^{n'-1}$ ,  $n' = k^{-1} = \sqrt{v_0/(v-v_0)}$  and

$$\text{constant} = -\frac{\sqrt{2}}{16\pi} \frac{n' q^4 S}{\sqrt{1 - \exp(-2\pi n')}} \dots \dots (27)$$

The transitions which give values different from zero can easily be seen from the following grouping:—

H <sub>2</sub>	S	S	S	S	A	A	A	A
H <sub>2</sub> <sup>+</sup> :e	S <sup>E</sup> A <sup>N</sup>	S <sup>E</sup> S <sup>N</sup>	A <sup>E</sup> S <sup>N</sup>	A <sup>E</sup> A <sup>N</sup>	S <sup>E</sup> A <sup>N</sup>	S <sup>E</sup> S <sup>N</sup>	A <sup>E</sup> S <sup>N</sup>	A <sup>E</sup> A <sup>N</sup>
Tran. Prob.	4I	0	0	0	0	0	-4I	0

In the above, S against H<sub>2</sub> denotes S<sup>E</sup>S<sup>N</sup> or A<sup>E</sup>A<sup>N</sup>, and A against H<sub>2</sub> denotes S<sup>E</sup>A<sup>N</sup> or A<sup>E</sup>S<sup>N</sup>. So that the only transitions which are non-zero are:

$$\begin{aligned}
 S \text{ or } \begin{cases} S^N S^E \\ A^N A^E \end{cases} \text{ of } H_2 &\longrightarrow S^E A^N \text{ of } H_2^+ \\
 A \text{ or } \begin{cases} A^E S^N \\ S^E A^N \end{cases} \text{ of } H_2 &\longrightarrow S^N A^E \text{ of } H_2^+.
 \end{aligned}$$

That is to say, transitions occur to antisymmetric states of  $H_2^+$  only. The transition-probability is now given by

$$M_{kk'}^e(z) = 4CC_2eI/q \text{ or } 4C'C_3eI/q \quad \dots \quad (28)$$

where I is given in (27).

So that the complete expression for  $M_{kk'}^e(z)$  is

$$-\frac{1}{8\sqrt{1\pm S^2}} \cdot \frac{1}{\sqrt{1\pm X^2\mp SY}} \frac{n'q^3S}{\sqrt{1-\exp(-2\pi n')}} \cdot \frac{1}{4\pi} \oint_{\xi} \int_{-1}^1 \int_{-1}^1 \exp(-\frac{1}{2}\lambda q(1+2ik\xi)) \cdot \exp(-\frac{1}{2}\mu q(1-2ik\xi)) \cdot \lambda\mu(\lambda+\mu)(\xi+\frac{1}{2})^{-n'-1}(\xi-\frac{1}{2})^{n'-1} d\xi d\lambda d\mu \quad \dots \quad (29)$$

We have next to find out the values of X, Y and J, given by:

$$X = \int u(a1)_{1s} u(b1)_{cs} d\Omega_1; \quad Y = \int u(a1)_{cs} u(b1)_{cs} d\Omega_1;$$

$$J = \oint \int \int \exp(-\frac{1}{2}\lambda q(1+2ik\xi)) \exp(-\frac{1}{2}\mu q(1-2ik\xi)) \lambda\mu(\lambda+\mu) \cdot F(\xi) d\lambda d\mu d\xi,$$

where the value of  $F(\xi)$  has been given *ante*.

The solution of X is given in Note 2(a), p. 105, and that of J, in Note 2(b), p. 107. As regards Y we observe that if we replace  $u(b, 1)_{cs}$  by  $u(a, 1)_{cs}$  then the integral reduces to  $\int [u(a1)_{cs}]^2 d\Omega_1$ . This integration cannot be carried out rigorously, for the exact  $\psi$ -function must be replaced by the asymptotic wave-function (vide Bethe, *Handbuch der Physik*, Vol. 24) for the continuous state which holds for large distance from the nucleus. This simplified function is then normalized for a small finite range of energy  $\Delta E$ . The asymptotic wave-function holds for distances where  $1/r^2$  can be neglected in comparison with  $1/r$  (i.e.  $1/r \gg 1/r^2$ ). At such distances one can notice that  $r_{a1}$  and  $r_{b1}$  will be almost identical, for then  $q$  is very small compared to either of them. Hence we may replace  $r_{a1}$  for  $r_{b1}$  in the wave-function. Thus the integral

$$Y = \int u(a1)_{cs} u(b1)_{cs} d\Omega_1 \quad \dots \quad (30)$$

can be given the asymptotic form  $\approx \int u(a1)_{cs} u(a1)_{cs} d\Omega_1$ .

Since  $u(a, 1)_{cs}$  is already the normalized eigen-function the integral Y has the value unity. We have thus

$$M_{kk'}^e(z) = 2CC_2 ek(2J)/q \text{ or } 2C'C_3 ek(2J)/q \\ = -\frac{1}{\sqrt{1\pm S^2}} \cdot \frac{1}{\sqrt{1\pm X^2\mp SY}} \cdot \frac{eq^3S}{32\pi} \cdot \frac{n'J}{\sqrt{1-\exp(-2\pi n')}} \quad \dots \quad (31)$$

The evaluation of the integral J has been given in Note 2(b); so we quote here its value.

$$J = \exp(-2n' \cot^{-1} n') \left[ \frac{4\pi n'}{1+n'^2} G_1(q) + \frac{4\pi n'^3}{(1+n'^2)^2} G_2(q) \right] \quad \dots \quad (32)$$

where  $G_1(q) = 8(1/q^2 + 6/q^4) \cosh q - 24(1/q^3 + 8/q^5) \sinh q$ ,  
 $G_2(q) = -32(1/q^4 \cdot \cosh q + 1/q^5 \cdot \sinh q)$ .

The complete expression for the electronic transition probability is given below:

$$M_{kk'}^e(z) = -\frac{1}{\sqrt{1 \pm S^2}} \cdot \frac{1}{\sqrt{1 \pm X^2 \mp S}} \cdot \frac{eS \exp(-2n' \cot^{-1} n')}{\sqrt{1 - \exp(-2\pi n')}} \times$$

$$\times \left[ \frac{n'^2}{1+n'^2} \left\{ \left( q + \frac{6}{q} \right) \cosh q - 3 \left( 1 + \frac{2}{q^2} \right) \sinh q \right\} \right.$$

$$\left. + \left( \frac{n'^2}{1+n'^2} \right)^2 \left\{ -\frac{4}{q} \cosh q + \frac{4}{q^2} \sinh q \right\} \right].$$

$$= \frac{eS \exp(-2n' \cot^{-1} n')}{\sqrt{(1 \pm S^2)(1 \pm X^2 \mp S)(1 - \exp(-2\pi n'))}} \left[ \left( \frac{\nu_0}{\nu} \right) \left\{ \left( q + \frac{6}{q} \right) \cosh q \right. \right.$$

$$\left. - 3 \left( 1 + \frac{2}{q^2} \right) \sinh q \right\} + \left( \frac{\nu_0}{\nu} \right)^2 \left\{ -\frac{4}{q} \cosh q + \frac{4}{q^2} \sinh q \right\} \right] \dots \quad (33)$$

where

$$S = (1 + 2q + q^2/3) \exp(-q),$$

$$X = -\frac{2n'^2}{1+n'^2} \sqrt{\frac{2}{1 - \exp(-2\pi n')}} \left( \cosh q - \frac{1}{q} \sinh q \right).$$

Hence, for electronic transition,  $\tau(\nu)$  is given by

$$\tau(\nu) = \frac{8\pi^3 \nu}{c} \left| M_{kk'}^e \right|^2$$

$$= \frac{8\pi^3 \nu e^2 S^2 \exp(-4n' \cot^{-1} n')}{c[(1 \pm S^2)(1 \pm X^2 \mp S)(1 - \exp(-2\pi n'))]} \left\{ \left( \frac{\nu_0}{\nu} \right)^2 G_{11}^2(q) + 2 \left( \frac{\nu_0}{\nu} \right)^3 G_{12}(q) \right.$$

$$\left. + \left( \frac{\nu_0}{\nu} \right)^4 G_{22}^2(q) \right\} \dots \dots \dots \dots \dots \dots \dots \quad (34)$$

where

$$\begin{cases} G_{11}(q) = (q + 6/q) \cosh q - 3(1 + 2/q^2) \sinh q, \\ G_{22}(q) = -4 \cosh q/q + 4 \sinh q/q^2, \quad G_{12}(q) \equiv G_{11}(q)G_{22}(q), \\ \nu_0/\nu = n'^2/(1+n'^2), \quad n' = \sqrt{\nu_0/(\nu - \nu_0)}. \end{cases}$$

or

$$\tau(\nu) = \frac{8\pi^3 \nu e^2 S^2 \exp(-4n' \cot^{-1} n')}{c[(1 \pm S^2)(1 \pm X^2 \mp S)(1 - \exp(-2\pi n'))]} \left\{ 0.777 \left( \frac{\nu_0}{\nu} \right) - 2.2038 \left( \frac{\nu_0}{\nu} \right)^2 \right\}$$

.. (34-1)

for  $q = 1.418$ ,  $\cosh q = 2.17$  and  $\sinh q = 1.92$ .

We can now compare the value of  $\tau(\nu)$  for the electron-transition  $1s^2 \rightarrow 1s\sigma s$  with that for the H-atom  $1s \rightarrow \infty p$ . For the last, we have according to Bethe (1936):

$$\tau(\nu) = \frac{2^8 \pi e^2 \nu_0^3 \exp(-4n' \cot^{-1} n')}{3 mc \nu^4 (1 - \exp(-2\pi n'))} \dots \dots \quad (35)$$

For the threshold frequency, we have  $\nu = \nu_0$  and

$$\tau_0 = \frac{2^8 \pi e^2 \epsilon^{-4}}{3 mc \nu_0} = 1.26 \times 10^{-17} \text{ cm}^2.$$

For the electronic part of the molecular transition, we have, according to (34.1)

$$\tau(\nu) = \frac{8\pi^3 \nu e^2}{c} \frac{2a^3}{e^2} \left\{ \left( \frac{\nu_0}{\nu} \right) G_{11} + \left( \frac{\nu_0}{\nu} \right)^2 G_{22} \right\}^2 Q. \quad \dots \quad (36)$$

Here we have written  $\tau(\nu)$  in usual C.G.S. units in place of Hartree units in which  $\tau(\nu)$  in (34) has been expressed. For this it has been necessary to multiply (34.1) by  $2a^3/e^2$ , where 'a' is the Bohr-radius, '2' representing the number of electrons capable of making the transition. By 'Q' we denote the complicated expression:—

$$\frac{S^2}{(1 \pm S^2)(1 \pm X^2 \mp S)} \cdot \frac{\exp(-4n' \cot^{-1} n')}{1 - \exp(-2\pi n')}.$$

Now it can be shown after some work that the above expression reduces to

$$\tau(\nu) = \frac{\pi e^2}{mc} \left( \frac{\nu_0}{\nu_1} \right)^2 \frac{1}{\nu_0} \left( G_{11} + \left( \frac{\nu_0}{\nu} \right) G_{22} \right)^2 Q, \quad \dots \quad (37)$$

where  $\nu_1 = \text{Rydberg frequency} = 2\pi^2 e^4 m / h^3$ .

This expression may be contrasted with (35). Let us compare their threshold values. At  $\nu = \nu_0$ , we have for the ionization of  $H_2$  to  $H_2^+$

$$\tau_0 = \frac{\pi e^2}{mc} \left( \frac{\nu_0}{\nu_1} \right)^2 \frac{1}{\nu_0} (G_{11} + G_{22})^2 \epsilon^{-4} \left\{ \frac{S^2}{(1+S^2)(1+X^2-S)} \right\}. \quad \dots \quad (38)$$

Now we have

$$(G_{11} + G_{22})^2 = (-1.524)^2 = 2.26,$$

$$S^2/(1+S^2)(1+X^2-S) = 1.233,$$

$$\nu_0/\nu_1 = 124569/109765 = 1.135.$$

From these figures, we obtain for ionization of  $H_2$

$$\tau_0 = \frac{\pi e^2}{mc} \frac{1}{\nu_1} \epsilon^{-4} [1.135 \times 1.233 \times 2.325] = (3.252) \frac{\pi e^2 \epsilon^{-4}}{mc \nu_1}. \quad \dots \quad (38.1)$$

We have, therefore,  $\tau_0$  for the process  $H_2 \rightarrow H_2^+$  :  $\tau_0$  for  $H \rightarrow H^+ = 3.252 : 28/3 = 3.8 \times 10^{-2}$ , i.e., the molecular process is nearly 25 times weaker.

This is as is otherwise expected, for the process  $1s^2 \rightarrow 1s\cos$  should necessarily be rather feeble. The main process would be from  $1s^2 \rightarrow 1s\cos p$ . The value of  $\tau(\nu)$  for this process is very difficult to calculate, but it is being carried out, with no definite result to report at present. Of course, this value of  $\tau(\nu)$  for molecular ionization would be further reduced on account of the value of  $M_{kk}^2$  (vide *infra*).

## 4. TRANSITION-PROBABILITY DUE TO VIBRATION

Let us now calculate the vibrational part of  $|M_{kk'}|$ , viz.,

$$\int \psi_1(V'; q_1) \psi_2(V''; q_2) d\Omega_v.$$

Here  $\psi_1(V'; q_1)$  refers to the vibrational state of the  $H_2^+$ -molecule,  $V'$  being the quantum number of the particular vibrational state to which  $H_2^+$  is raised by absorption of light. We write  $\psi_1(V'; q_1)$  for  $H_2^+$  ion,  $q_1$  being the nuclear distance. Similarly,  $\psi_2(V''; q_2)$  refers to the  $H_2$ -molecule. Now we have (vide Pauling and Wilson's 'Quantum Mechanics', 1935, p. 107)

$$\psi_1(V'; q_1) = N_{V'} \exp(-\beta_1 q_1^2/2) H_{V'}(\sqrt{\beta_1} q_1) \quad \dots \quad (39)$$

where  $q_1 = q - q_0'$ , where  $q$  is the separation between the component nuclei,  $q_0'$  = normal distance between the nuclei in  $H_2^+$ ,  $\beta_1 = 4\pi^2 \mu \omega_0'/h$ ,  $\mu$  being the reduced mass (=  $M/2$ ,  $M$  is the mass of the  $H$ -atom),  $\omega_0'$  is the fundamental vibrational frequency of  $H_2^+$ . Further,

$$N_{V'} = \left[ \frac{1}{2^{V'} \cdot V'!} \sqrt{\frac{\beta_1}{\pi}} \right]^{\frac{1}{2}} \quad \dots \quad (40)$$

In a similar way, it can be shown that

$$\psi_2(V''; q_2) = N_{V''} \exp(-\beta_2 q_2^2/2) \cdot H_{V''}(\sqrt{\beta_2} q_2) \quad \dots \quad (41)$$

where  $\beta_2 = 4\pi^2 \mu \omega_0''/h$ ,  $q_2 = q - q_0''$ ,  $q_0''$  = separation between nuclei in  $H_2$ , and  $N_{V''}$  has a value similar to (40). We then have

$$|M_{kk'}^v| = \int \psi_1(V'; q_1) \psi_2(V''; q_2) dq \quad \dots \quad (42)$$

The evaluation of integrals of type (42) has been carried out by Hutchisson (1930), but his expressions have been given in too much condensed form for any numerical calculation. We therefore work out the integral (42) in detail.

Let us put  $\omega_0''/\omega_0' = \alpha^2$ .

Further, as we have observed, since  $q_2 = q - q_0''$ , and  $q_1 = q - q_0'$ , where  $q$  is the running co-ordinate representing the distance between the nuclei, and  $q_0''$ ,  $q_0'$  are the nuclear distances for  $H_2$  and  $H_2^+$ , we have

$$q_2 = q_1 + q_0' - q_0''$$

and

$$\sqrt{\beta_2} q_2 = \sqrt{\beta_2} (q_1 + q_0' - q_0'') = \alpha \eta + \delta$$

where

$$\eta = \sqrt{\beta_1} q_1, \quad \delta = \sqrt{\beta_2} (q_0' - q_0'').$$

We have therefore for the integral (42) to denote here by the symbol  $I_{V'V''}$ :

$$I_{V'V''} = \left[ \frac{1}{2^{V'+V''} \cdot V'! V''!} \right]^{\frac{1}{2}} \left( \frac{4\pi\mu}{h} \right)^{\frac{1}{2}} (\omega_0' \omega_0'')^{\frac{1}{2}} \beta_1^{-\frac{1}{2}} \{I\}, \quad \dots \quad (42.1)$$

where

$$\{I\} = \int_{-\infty}^{\infty} \exp(-\frac{1}{2}\eta^2) \exp(-\frac{1}{2}(\alpha\eta + \delta)^2) H_{V'}(\eta) H_{V''}(\alpha\eta + \delta) d\eta \quad \dots \quad (43)$$

The occurrence of  $\beta_1^{-\frac{1}{2}}$  in (42.1) is due to the fact that  $d\Omega_v = dq$ , and  $dq = d\eta/\sqrt{\beta_1}$ .

After a little work, we obtain

$$I_{V'V''} = \left[ \frac{\alpha/\pi}{2^{V'+V''} V'! V''!} \right]^{\frac{1}{2}} \{I\} \dots \dots \dots (44)$$

The integral  $\{I\}$  has been worked out by Hutchisson, and it is useless to repeat the results. We are concerned only with the case where  $V'' = 0$ . It can be shown after some work that

$$I_{00} = \sqrt{\frac{2\alpha}{1+\alpha^2}} \exp(-\delta^2/2(1+\alpha^2)) \dots \dots (44.1)$$

and the ratios  $I_{V'0}/I_{00}$  are shown in the following table.

TABLE I.

$V''$	$V'$	$I_{V'0}/I_{00}$
0	1	$\frac{1}{\sqrt{2}} d_1$
0	2	$\frac{1}{\sqrt{2}} (d_2 + b_2)$
0	3	$\sqrt{\frac{3}{4}} (d_3 + b_2 d_1)$
0	4	$\sqrt{\frac{3}{2}} (d_4 + b_2 d_2 + b_4)$
0	5	$\sqrt{\frac{15}{4}} (d_5 + b_2 d_3 + b_4 d_1)$
.	.	.....
.	.	.....
.	.	.....
0	$n$	$\sqrt{\frac{n!}{2^{n/2}}} (d_n + b_2 d_{n-2} + b_4 d_{n-4} + \dots)$

where

$$d_x = \left( \frac{2\alpha x}{1+\alpha^2} \right)^x, \quad b_y = \left( \frac{1-\alpha^2}{1+\alpha^2} \right)^{y/2},$$

$y$  being even-numbered, and  $x$  any integral, even or odd.

*Numerical Calculation.*

We have now

$$q_0'' = 0.749 \text{ \AA.U.}, \quad q_0' = 1.070 \text{ \AA.U.},$$

$$\omega_0'' = 4275 \text{ cm}^{-1}, \quad \omega_0' = 2235 \text{ cm}^{-1}.$$

$$\begin{aligned}
 \text{Hence} \quad \alpha &= (\omega_0''/\omega_0')^{\frac{1}{2}} = 1.3812 \\
 &= \sqrt{\frac{4\pi^2\mu\omega_0''}{h}} (q_0' - q_0'') \\
 &= 0.1221(q_0' - q_0'')(M\omega_0'')^{\frac{1}{2}},
 \end{aligned}$$

where  $q_0'$ ,  $q_0''$  are expressed in Angstrom, M with O = 16,  $\omega_0''$  in  $\text{cm}^{-1}$ .

We easily verify that, for the present case,  $\delta = 2.56$ . With the aid of these values, we can calculate  $d_x$  and  $b_y$  and then calculate the numerical value of  $I_{V'0}$ , for integral values of  $V'$ . These are shown in Tables (II) and (III).

We have further  $I_{00} = 1.7552 \times 10^{-1}$ .

TABLE II.

$b_0 = 1.00000$	$d_0 = 1.00000$	$d_5 = -0.68172$
$b_2 = -0.31210$	$d_1 = -2.41300$	$d_6 = 0.27416$
$b_4 = 0.04873$	$d_2 = 2.91130$	$d_7 = -0.09450$
$b_6 = -0.00606$	$d_3 = -2.34163$	$d_8 = 0.02850$
$b_8 = 0.00039$	$d_4 = 1.41260$	$d_9 = -0.00764$

TABLE III.

$V''$	$V'$	$I_{V'0}/I_{00} = M_{kk'}^v/I_{00}$	$M_{kk'}^v$	$ M_{kk'}^v ^2$
0	0	1.0000	$1.7552 \times 10^{-1}$	$3.0807 \times 10^{-2}$
0	1	-1.7113	$-3.0037 \times 10^{-1}$	$9.0222 \times 10^{-2}$
0	2	1.8381	$3.2262 \times 10^{-1}$	$10.4084 \times 10^{-2}$
0	3	-1.3757	$-2.4146 \times 10^{-1}$	$5.8303 \times 10^{-2}$
0	4	0.6769	$1.1881 \times 10^{-1}$	$1.4116 \times 10^{-2}$
0	5	-0.1325	$-0.2326 \times 10^{-1}$	$0.0541 \times 10^{-2}$
0	6	-0.1039	$-0.1824 \times 10^{-1}$	$0.0333 \times 10^{-2}$
0	7	0.1178	$0.2068 \times 10^{-1}$	$0.0428 \times 10^{-2}$
0	8	-0.0744	$-0.1306 \times 10^{-1}$	$0.0171 \times 10^{-2}$

## 5. CONCLUSION

We can now get a qualitative idea regarding the nature of the complete absorption curve  $\tau(\nu)/\nu$ . Referring back to (2), (6), (34.1) and (44), and

putting  $[\psi_1(m)\psi_2(m)d\phi]^2$  equal to unity, as can be easily verified, we have

$$\tau_{\nu}^{+} = \frac{8\pi^3 e^2 \nu_0}{c} L(\nu) F(X, S) \Phi^2(\nu) I_{V'V''}^2,$$

$$\tau_{\nu}^{-} = \frac{8\pi^3 e^2 \nu_0}{c} L(\nu) F^*(X, S) \Phi^2(\nu) I_{V'V''}^2,$$

where  $L(\nu)$ ,  $F(X, S)$ ,  $F^*(X, S)$ ,  $\Phi(\nu)$  are quantities defined in Tables IV to X given in the Appendix.

We observe from the tables (VII), (VIII), that  $F(X, S)$ ,  $F^*(X, S)$  are slowly varying functions. When  $\nu = \nu_0$ ,  $F(X, S) = 1.2330$ ; when  $\nu = 2\nu_0$ , it is 1.3150. But we have, in practice, to plot the  $\tau(\nu)/\nu$  curve close to  $\nu = \nu_0$ ; hence it is convenient to take this quantity as constant, say 1.25. Similarly,  $1 - \exp(-2\pi n')$  also varies slowly for this region. The main variation is in  $\Phi(\nu)$ . We observe that  $\Phi(\nu)$  becomes zero at a certain frequency near  $\nu = 3\nu_0$ , and after that slowly rises. This is a somewhat unexpected result, but in actual practice we have not to go so far, because absorption will be mostly confined to the neighbourhood of  $\nu = \nu_0$ .

Since  $\nu = \nu_e + (V' + \frac{1}{2})\omega_0' - (V'' + \frac{1}{2})\omega_0''$ , neglecting rotation, and since  $V'' = 0$ , we have  $\nu = 123569 + \frac{1}{2}(\omega_0' - \omega_0'') + V'\omega_0' = \nu_0 + \omega_0' V' = 123549 + \omega_0' V'$ . We get then  $\nu_0 = 123549$ , and the stretch from  $\nu = \nu_0$  to  $\nu = 2\nu_0$  contains about 56  $\omega_0'$ . We shall see presently, since the value of  $I_{V_0}$  jumps suddenly at each point  $\nu = \nu_0 + \omega_0' V'$ , where  $V' = 1, 2, 3, \dots$ , and after  $V' = 3$ , the value of  $I_{V_0}$  drops suddenly, the possible zero value of  $\Phi(\nu)$  at  $\nu = 3\nu_0$  roughly is far outside the region we are contemplating. The actual calculations are shown in Table X, and finally in Table XI, and the form of the  $\tau(\nu)/\nu$ -curve is represented in Fig. 2.

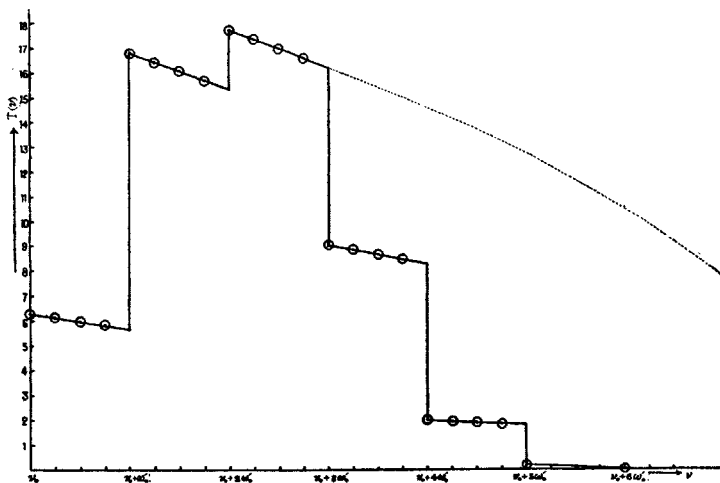


FIG. 2.



We observe from this, that the absorption curve behaves exactly in the way mentioned at the end of §1. The maximum value of  $\tau(\nu)$  is not reached at  $\nu = \nu_0$ , but at  $\nu = \nu_0 + 2\omega_0'$ , where it is about three times larger than the value at  $\nu = \nu_0$ . At each vibrational number there is a sudden jump, *up* before  $\nu = \nu_0 + 2\omega_0'$  and *down* after  $\nu = \nu_0 + 2\omega_0'$ . It therefore appears that after  $\nu = \nu_0 + 3\omega_0'$ , the continuous absorption, which raises  $\text{H}_2^+$  to the third vibrational level, and leaves the rest of the energy to the electron, is more probable than raising  $\text{H}_2^+$  to a higher vibrational level. So this part of the curve is drawn up to some distance and is shown by dots.

As the actual absorption curve  $\tau(\nu)/\nu$  leading to photo-dissociation will correspond to the process  $\text{I s}^2 \rightarrow \text{I s} \infty p$  no attempt has been made to obtain further conclusions, particularly as the experimental results are very meagre.

Lastly, we have great pleasure in acknowledging our gratefulness to Prof. M. N. Saha, F.R.S., for his inspiring guidance and the keen interest he has shown in the several stages of this work.

#### Note 1.

To show that the various integrals contained in

$$\begin{aligned} \mathbf{M}(z) = \frac{CC_1 e}{q} \iint (\psi_1' + \psi_2') [(r_{a1}^2 - r_{b1}^2) + (r_{a2}^2 - r_{b2}^2)] \times \\ \times (\psi(1) + \psi(2) + \psi(3) + \psi(4)) d\Omega_1 d\Omega_2 \end{aligned}$$

either reduce to zero or to the form:

$$\mathbf{I} = S \int u(a1)_{1s} u(b1)_{cs} (r_{a1}^2 - r_{b1}^2) d\Omega_1.$$

We take each of the products in (25) and multiply by the electric moment  $[\mathbf{M}(z_1) + \mathbf{M}(z_2)]$  and integrate over the co-ordinate spaces of the electrons.

Since A and G differ only in an interchange of nuclei, the integrals obtained from the product of the electric moment and A or G will be either equal, or equal except for a change of sign, according as there is, or is not, a change in the nuclear symmetry during the transition. A similar argument holds for an interchange of electrons as between A and F, and D and G. This shows that the expressions A, D, F and G when integrated after multiplication with the electric moment will have the same absolute value. In an exactly similar manner it may be concluded that B, H, C and E will have the same absolute value. It is presently shown that the integral  $\int A[\mathbf{M}]d\Omega = 0$ . Hence the integrals obtained from D, F and G are also zero.

$$\begin{aligned} \int A[\mathbf{M}]d\Omega &= \int \psi_1' \psi(1) [\mathbf{M}(z_1) + \mathbf{M}(z_2)] d\Omega \\ &= \int u(b2)_{1s} u(b2)_{cs} d\Omega_2 \cdot \int u(a1)_{1s} (r_{a1}^2 - r_{b1}^2) u(a1)_{1s} d\Omega_1 \\ &\quad + \int [u(a1)_{1s}]^2 d\Omega_1 \cdot \int u(b2)_{1s} (r_{a2}^2 - r_{b2}^2) u(b2)_{cs} d\Omega_2. \end{aligned}$$

Remembering  $\int u(b2)_{1s} u(b2)_{cs} = 0$ , due to orthogonality, and using elliptic co-ordinates defined by

$$\lambda = (r_{a2} + r_{b2})/q, \mu = (r_{a2} - r_{b2})/q, d\Omega = \frac{1}{8} q^8 (\lambda^2 - \mu^2) d\lambda d\mu d\phi,$$

we get

$$u(b2)_{1s} = \frac{1}{\sqrt{\pi}} \exp(-\frac{1}{2}q(\lambda - \mu)),$$

and

$$u(b2)_{cs} = -\sqrt{\frac{2}{1 - \epsilon^{-2\pi n'}}} \cdot \frac{n'}{q(\lambda - \mu)} \cdot \frac{1}{2\pi} \oint_{\xi} \exp(-iqk\xi(\lambda - \mu)) F(\xi) d\xi.$$

The integral now assumes the form :

$$\text{Const.} \oint_{\xi} \int_{-1}^{\infty} \int_{-1}^1 \exp(-\frac{1}{2}\lambda q(1 + 2ik\xi)) \exp(\frac{1}{2}\mu q(1 + 2ik\xi)) \times \\ \times \lambda \mu (\lambda + \mu) (\xi + \frac{1}{2})^{-m'-1} (\xi - \frac{1}{2})^{m'-1} d\xi d\lambda d\mu.$$

A factor of the above integral is the following :—

$$\int_{-1}^{\infty} \int_{-1}^1 \lambda \mu (\lambda + \mu) \exp(-\frac{1}{2}\lambda q(1 + 2ik\xi)) \exp(\frac{1}{2}\mu q(1 + 2ik\xi)) d\lambda d\mu,$$

whose value is  $4/q^2(1 + 2ik\xi)^2$ , for this = A'B' + C'D', where

$$A' = \int_{-1}^{\infty} \lambda^2 \exp(-\lambda a) d\lambda = \epsilon^{-a}(1/a + 2/a^2 + 2/a^3); \quad (a = \frac{1}{2}q(1 + 2ik\xi)).$$

$$B' = \int_{-1}^1 \mu \exp(\mu a) d\mu = (\epsilon^a + \epsilon^{-a})/a - (\epsilon^a - \epsilon^{-a})/a^2;$$

$$C' = \int_{-1}^{\infty} \lambda \exp(-\lambda a) d\lambda = \epsilon^{-a}(1/a + 1/a^2);$$

$$D' = \int_{-1}^1 \mu^2 \exp(\mu a) d\mu = (\epsilon^a - \epsilon^{-a})/a - 2[(\epsilon^a + \epsilon^{-a})/a - (\epsilon^a - \epsilon^{-a})/a^2]/a.$$

Hence the integral reduces to a contour integral

$$\text{Constant} \times \frac{4}{q^2} \oint_{\xi} (\xi + \frac{1}{2})^{-m'-1} (\xi - \frac{1}{2})^{m'-1} (1 + 2ik\xi)^{-2} d\xi,$$

with a pole at  $\xi = i/2k$ . The value of this = 0. (See Note 2(b).)

Thus integrals A, D, F and G all vanish.

We now take the integrals obtained from B, C, E and H. One can show by multiplying out and evaluating that

$$\int B[M]d\Omega = -\int C[M]d\Omega = \int E[M]d\Omega = -\int H[M]d\Omega.$$

Taking first the integral with B we get:—

$$\begin{aligned} & \int \psi_1' \psi(2) [M(z_1) + M(z_2)] d\Omega \\ &= \int u(a1)_{1s} u(b1)_{cs} (r_{1a}^2 - r_{b1}^2) d\Omega_1 \cdot \int u(a2)_{1s} u(b2)_{1s} d\Omega_2 + \\ & \quad \int u(a1)_{1s} u(b1)_{cs} d\Omega_1 \cdot \int u(a2)_{1s} u(b2)_{1s} (r_{a2}^2 - r_{b2}^2) d\Omega_2. \end{aligned}$$

Transforming

$$\int u(a2)_{1s} (r_{a2}^2 - r_{b2}^2) u(b2)_{1s} d\Omega_2$$

into elliptic co-ordinates defined above, we get it equivalent to

$$\begin{aligned} & \frac{q^5}{8\pi} \int_0^{2\pi} \int_1^\infty \int_{-1}^1 \lambda \mu (\lambda^2 - \mu^2) \exp(-\frac{1}{2}q(\lambda + \mu)) \exp(-\frac{1}{2}q(\lambda - \mu)) d\lambda d\mu d\phi \\ &= \frac{q^5}{4} \int_1^\infty \int_{-1}^1 \lambda \mu (\lambda^2 - \mu^2) \exp(-q\lambda) d\lambda d\mu = \frac{q^5}{4} [A''B'' - C''D''] = 0, \end{aligned}$$

for

$$A'' = \int_1^\infty \lambda^3 \exp(-q\lambda) d\lambda = \epsilon^{-q} (1/q + 3/q^2 + 6/q^3 + 6/q^4);$$

$$B'' = \int_{-1}^1 \mu d\mu = 0;$$

$$C'' = \int_1^\infty \lambda \exp(-q\lambda) d\lambda = \epsilon^{-q} (1/q + 1/q^2);$$

$$D'' = \int_{-1}^1 \mu^3 d\mu = 0.$$

Now

$$\int u(a2)_{1s} u(b2)_{1s} d\Omega_2$$

is our Suguira-integral S.

Hence the integral containing B

$$= S \int u(a1)_{1s} (r_{a1}^2 - r_{b1}^2) u(b1)_{cs} d\Omega_1 = SI^* = I$$

From E we have similarly a value = I; and from each of C and H the value -I.

*Note 2(a).*

To evaluate

$$X = \int u(a1)_{1s} u(b1)_{cs} d\Omega_1.$$

We have (See Bethe, *Handbuch der Physik*, Bd. 24, 1933, l.c.)

$$u(a1)_{1s} = \frac{1}{\sqrt{\pi}} \exp(-r_{a1});$$

$$u(b1)_{cs} = -\sqrt{\frac{2}{1-\epsilon-2\pi n'}} \cdot \frac{1}{2^{\frac{3}{2}} \pi^{\frac{3}{2}}} \cdot \frac{n'}{r_{b1}} \oint_{\xi} \exp(-2ikr_{b1}\xi) F(\xi) d\xi.$$

Transforming into elliptic co-ordinates the above eigen-functions become:

$$u(a1)_{1s} = \frac{1}{\sqrt{\pi}} \exp\left(\frac{-q}{2}(\lambda+\mu)\right);$$

$$u(b1)_{cs} = -\frac{1}{\sqrt{1-\epsilon-2\pi n'}} \cdot \frac{n'}{\pi^{\frac{3}{2}} \cdot 2^{\frac{3}{2}}} \cdot \frac{1}{q(\lambda-\mu)} \oint_{\xi} \exp(-ikq(\lambda-\mu)\xi) \cdot F(\xi) d\xi.$$

The integral X now takes the form:

$$X = -\frac{n'q^2}{16\pi} \sqrt{\frac{2}{1-\epsilon-2\pi n'}} \oint_{\xi} \int_1^{\infty} \int_{-1}^1 \exp(-\frac{1}{2}\lambda q(1+2ik\xi)) \times \\ \times \exp(-\frac{1}{2}\mu q(1-2ik\xi)) \cdot (\lambda+\mu) F(\xi) d\lambda d\mu d\xi.$$

Let us evaluate

$$J' = \oint_{\xi} \int_1^{\infty} \int_{-1}^1 \exp(-\frac{1}{2}\lambda q(1+2ik\xi)) \exp(-\frac{1}{2}\mu q(1-2ik\xi)) \cdot (\lambda+\mu) F(\xi) d\lambda d\mu d\xi.$$

$$\text{Call } J'' = \int_1^{\infty} \int_{-1}^1 \exp(-a\lambda) \exp(-b\mu) \cdot (\lambda+\mu) d\lambda d\mu,$$

where

$$a = \frac{1}{2}q(1+2ik\xi), \quad b = \frac{1}{2}q(1-2ik\xi).$$

$$\therefore J'' = (\epsilon^b - \epsilon^{-b}) \{I\} / b + \epsilon^{-a} \{III\} / a,$$

where

$$\{I\} = \int_1^{\infty} \lambda \exp(-a\lambda) d\lambda = \epsilon^{-a} (1/a + 1/a^2);$$

$$\{III\} = \int_{-1}^1 \mu \exp(-b\mu) d\mu = \epsilon^b (-1/b + 1/b^2) - \epsilon^{-b} (1/b + 1/b^2).$$

Whence

$$J'' = \epsilon^{-(a-b)} \cdot (1/a^2b + 1/ab^2) - \epsilon^{-(a+b)} \cdot (2/ab + 1/a^2b + 1/ab^2) \\ = \epsilon^{-2qk\xi} [8/q^3(1+2ik\xi)^2(1-2ik\xi) + 8/q^3(1+2ik\xi)(1-2ik\xi)^2] \\ - \epsilon^{-q} [8/q^2(1+2ik\xi)(1-2ik\xi) + 8/q^3(1+2ik\xi)^2(1-2ik\xi) \\ + 8/q^3(1+2ik\xi)(1-2ik\xi)^2].$$

Splitting up into partial fractions (see a list in the body of Note 2(b)) and rearranging we get

$$\begin{aligned}
J' = & h_1 \oint_{\xi} (1+2ik\xi)^{-1} F(\xi) d\xi + h_{-1} \oint_{\xi} (1-2ik\xi)^{-1} F(\xi) d\xi + h_2 \oint_{\xi} (1+2ik\xi)^{-2} F(\xi) d\xi \\
& + h_{-2} \oint_{\xi} (1-2ik\xi)^{-2} F(\xi) d\xi + h_1' \oint_{\xi} (1+2ik\xi)^{-1} F(\xi) \exp(-2q\xi/n') d\xi \\
& + h_{-1}' \oint_{\xi} (1-2ik\xi)^{-1} F(\xi) \exp(-2q\xi/n') d\xi \\
& + h_2' \oint_{\xi} (1+2ik\xi)^{-2} F(\xi) \exp(-2q\xi/n') d\xi \\
& + h_{-2}' \oint_{\xi} (1-2ik\xi)^{-2} F(\xi) \exp(-2q\xi/n') d\xi,
\end{aligned}$$

where

$$\begin{aligned}
h_1 & \equiv h_{-1} = -4\epsilon^{-q}(1/q^2+1/q^3); \\
h_2 & \equiv h_{-2} = -4\epsilon^{-q}/q^3; \\
h_1' & \equiv h_{-1}' = 4/q^3; \\
h_2' & \equiv h_{-2}' = 4/q^3.
\end{aligned}$$

Quoting the values of the contour integrals (given in Note 2(b)) we derive after simplifications:—

$$J' = \frac{32\pi n'}{1+n'^2} (\cosh q/q^2 - \sinh q/q^3) \exp(-2n' \cot^{-1} n'),$$

$$X = -\frac{2n'^2}{1+n'^2} \sqrt{\frac{2}{1-\epsilon^{-2\pi n'}}} (\cosh q - \sinh q/q) \exp(-2n' \cot^{-1} n').$$

Note 2(b).

To evaluate

$$\begin{aligned}
J = \oint_{\xi} \int_1^{\infty} \int_{-1}^1 \exp(-\frac{1}{2}\lambda q(1+2ik\xi)) \exp(-\frac{1}{2}\mu q(1-2ik\xi)) \cdot \lambda\mu(\lambda+\mu) \times \\
\times F(\xi) d\lambda d\mu d\xi,
\end{aligned}$$

where  $F(\xi) = (\xi+\frac{1}{2})^{-m'-1} (\xi-\frac{1}{2})^{m'-1}$ , ( $k = 1/n'$ ).

Call  $J_1 = \int_1^{\infty} (\lambda^2\mu + \lambda\mu^2) \exp(-\frac{1}{2}q\lambda(1+2ik\xi)) d\lambda = \mu^2 \{I\} + \mu \{II\}$ ;

where  $\{I\} = \int_1^{\infty} \lambda \exp(-a\lambda) d\lambda = \epsilon^{-a}(1/a+1/a^2)$ ;  $a = \frac{1}{2}q(1+2ik\xi)$

$\{II\} = \int_1^{\infty} \lambda^2 \exp(-a\lambda) d\lambda = \epsilon^{-a}(1/a+2/a^2+2/a^3)$ .

$$\text{Next, call } J_2 = \int_{-1}^1 [\mu^2 \{I\} + \mu \{II\}] \exp(-b\mu) d\mu; \quad b = \frac{1}{2}q(1-2ik\xi) \\ = \{I\} \times \{IV\} + \{II\} \times \{III\},$$

$$\text{where } \{III\} = \int_{-1}^1 \mu \exp(-b\mu) d\mu = \epsilon^b(-1/b+1/b^2) - \epsilon^{-b}(1/b+1/b^2);$$

$$\{IV\} = \int_{-1}^1 \mu^2 \exp(-b\mu) d\mu \\ = \epsilon^b(1/b-2/b^2+2/b^3) - \epsilon^{-b}(1/b+2/b^2+2/b^3).$$

$$\therefore J_2 = -\epsilon^{-(a+b)}[2ab+3/a^2b+3/ab^2+4/a^2b^2+2/a^3b+2/ab^3+2/a^2b^3+2/a^3b^2] \\ + \epsilon^{-(a-b)}[-1/a^2b-1/ab^2+2/ab^3-2/a^3b+2/a^2b^3+2/a^3b^2].$$

Since  $a+b = q$ ,  $a-b = 2qik\xi$ , we write the expression for  $J_2$  in full; thus

$$J_2 = -\epsilon^{-q}[8/q^2(1+2ik\xi)(1-2ik\xi)+24/q^3(1+2ik\xi)^2(1-2ik\xi) \\ +24/q^3(1+2ik\xi)(1-2ik\xi)^2+64/q^4(1+2ik\xi)^2(1-2ik\xi)^2 \\ +32/q^4(1+2ik\xi)^3(1-2ik\xi)+32/q^4(1+2ik\xi)(1-2ik\xi)^3 \\ +64/q^5(1+2ik\xi)^2(1-2ik\xi)^3+64/q^5(1+2ik\xi)^3(1-2ik\xi)^2] \\ + \epsilon^{-2qik\xi}[-8/q^3(1+2ik\xi)^2(1-2ik\xi)-8/q^3(1+2ik\xi)(1-2ik\xi)^2 \\ -32/q^4(1+2ik\xi)^3(1-2ik\xi)+32/q^4(1+2ik\xi)(1-2ik\xi)^3 \\ +64/q^5(1+2ik\xi)^2(1-2ik\xi)^3+64/q^5(1+2ik\xi)^3(1-2ik\xi)^2].$$

Next we shall have to split up each term into partial fractions. We write down below the results of splitting up, putting  $x = 2ik\xi$  for short:—

$$f_0 = 1/(1+x)(1-x) = \frac{1}{2}/(1+x) + \frac{1}{2}/(1-x); \\ f_1 = 1/(1+x)^2(1-x) = \frac{1}{2}/(1+x)^2 + \frac{1}{4}/(1+x) + \frac{1}{4}/(1-x); \\ f_2 = 1/(1+x)(1-x)^2 = \frac{1}{2}/(1-x)^2 + \frac{1}{4}/(1-x) + \frac{1}{4}/(1+x); \\ f_3 = 1/(1+x)^3(1-x) = \frac{1}{2}/(1+x)^3 + \frac{1}{4}/(1+x)^2 + \frac{1}{8}/(1+x) + \frac{1}{8}/(1-x); \\ f_4 = 1/(1+x)(1-x)^3 = \frac{1}{2}/(1-x)^3 + \frac{1}{4}/(1-x)^2 + \frac{1}{8}/(1-x) + \frac{1}{8}/(1+x); \\ f_5 = 1/(1+x)^3(1-x)^2 = \frac{1}{4}/(1+x)^3 + \frac{1}{4}/(1+x)^2 + \frac{1}{16}/(1+x) + \frac{1}{8}/(1-x)^2 + \frac{1}{16}/(1-x); \\ f_6 = 1/(1+x)^2(1-x)^3 = \frac{1}{4}/(1-x)^3 + \frac{1}{4}/(1-x)^2 + \frac{1}{16}/(1-x) + \frac{1}{8}/(1+x)^2 + \frac{1}{16}/(1+x); \\ f_7 = 1/(1+x)^2(1-x)^2 = \frac{1}{4}/(1+x)^2 + \frac{1}{4}/(1+x) + \frac{1}{4}/(1-x)^2 + \frac{1}{4}/(1-x).$$

Utilizing these equivalent expressions for  $f_0, f_1, \dots$  in the expression for  $J_2$  we can write it in full thus:

$$J_2 = -\epsilon^{-q} \left[ \frac{1}{q^2} \left( \frac{4}{(1+x)} + \frac{4}{(1-x)} \right) + \frac{1}{q^3} \left( \frac{12}{(1+x)^2} + \frac{6}{(1+x)} + \frac{6}{(1-x)} \right) \right. \\ \left. + \frac{1}{q^3} \left( \frac{12}{(1-x)^2} + \frac{6}{(1-x)} + \frac{6}{(1+x)} \right) + \frac{1}{q^4} \left( \frac{16}{(1+x)^2} + \frac{16}{(1+x)} + \frac{16}{(1-x)^2} + \frac{16}{(1-x)} \right) \right. \\ \left. + \frac{1}{q^4} \left( \frac{16}{(1+x)^3} + \frac{8}{(1+x)^2} + \frac{4}{(1+x)} + \frac{4}{(1-x)} \right) \right]$$

$$\begin{aligned}
& + \frac{1}{q^4} \left( \frac{16}{(1-x)^3} + \frac{8}{(1-x)^2} + \frac{4}{(1-x)} + \frac{4}{(1+x)} \right) \\
& + \frac{1}{q^5} \left( \frac{16}{(1-x)^3} + \frac{16}{(1-x)^2} + \frac{12}{(1-x)} + \frac{8}{(1+x)^2} + \frac{12}{(1+x)} \right) \\
& + \frac{1}{q^5} \left( \frac{16}{(1+x)^3} + \frac{16}{(1+x)^2} + \frac{12}{(1+x)} + \frac{8}{(1-x)^2} + \frac{12}{(1-x)} \right) \Big] \\
& + \epsilon^{-2qk\xi} \left[ -\frac{1}{q^3} \left( \frac{4}{(1+x)^2} + \frac{2}{(1+x)} + \frac{2}{(1-x)} \right) \right. \\
& - \frac{1}{q^3} \left( \frac{4}{(1-x)^2} + \frac{2}{(1-x)} + \frac{2}{(1+x)} \right) \\
& - \frac{1}{q^4} \left( \frac{16}{(1+x)^3} + \frac{8}{(1+x)^2} + \frac{4}{(1+x)} + \frac{4}{(1-x)} \right) \\
& + \frac{1}{q^4} \left( \frac{16}{(1-x)^3} + \frac{8}{(1-x)^2} + \frac{4}{(1-x)} + \frac{4}{(1+x)} \right) \\
& + \frac{1}{q^5} \left( \frac{16}{(1-x)^3} + \frac{16}{(1-x)^2} + \frac{12}{(1-x)} + \frac{8}{(1+x)^2} + \frac{12}{(1+x)} \right) \\
& \left. + \frac{1}{q^5} \left( \frac{16}{(1+x)^3} + \frac{16}{(1+x)^2} + \frac{12}{(1+x)} + \frac{8}{(1-x)^2} + \frac{12}{(1-x)} \right) \right].
\end{aligned}$$

Rearranging above we get finally:—

$$\begin{aligned}
J_2 = & [g_1/(1+2ik\xi) + g_{-1}/(1-2ik\xi) + g_2/(1+2ik\xi)^2 + g_{-2}/(1-2ik\xi)^2 \\
& + g_3/(1+2ik\xi)^3 + g_{-3}/(1-2ik\xi)^3] + \exp(-2qk\xi) [g_1'/(1+2ik\xi) + g_{-1}'/(1-2ik\xi) \\
& + g_2'/(1+2ik\xi)^2 + g_{-2}'/(1-2ik\xi)^2 + g_3'/(1+2ik\xi)^3 + g_{-3}'/(1-2ik\xi)^3],
\end{aligned}$$

where

$$\begin{aligned}
g_1 & \equiv g_{-1} = -\epsilon^{-q}(4/q^2 + 12/q^3 + 24/q^4 + 24/q^5); \\
g_2 & \equiv g_{-2} = -\epsilon^{-q}(12/q^3 + 24/q^4 + 24/q^5); \\
g_3 & \equiv g_{-3} = -\epsilon^{-q}(16/q^4 + 16/q^5); \\
g_1' & \equiv g_{-1}' = -4/q^3 + 24/q^5; \\
g_2' & = -4/q^3 - 8/q^4 + 24/q^5; \\
g_{-2}' & = -4/q^3 + 8/q^4 + 24/q^5; \\
g_3' & = -16/q^4 + 16/q^5; \quad g_{-3}' = 16/q^4 + 16/q^5.
\end{aligned}$$

The integral  $J$  now splits up into twelve contour integrals:—

$$\begin{aligned}
J = & g_1 \oint_{\xi} \frac{F(\xi)d\xi}{(1+2ik\xi)} + g_{-1} \oint_{\xi} \frac{F(\xi)d\xi}{(1-2ik\xi)} + g_2 \oint_{\xi} \frac{F(\xi)d\xi}{(1+2ik\xi)^2} + g_{-2} \oint_{\xi} \frac{F(\xi)d\xi}{(1-2ik\xi)^2} \\
& + g_3 \oint_{\xi} \frac{F(\xi)d\xi}{(1+2ik\xi)^3} + g_{-3} \oint_{\xi} \frac{F(\xi)d\xi}{(1-2ik\xi)^3} + g_1' \oint_{\xi} \frac{H(\xi)d\xi}{(1+2ik\xi)} + g_{-1}' \oint_{\xi} \frac{H(\xi)d\xi}{(1-2ik\xi)} \\
& + g_2' \oint_{\xi} \frac{H(\xi)d\xi}{(1+2ik\xi)^2} + g_{-2}' \oint_{\xi} \frac{H(\xi)d\xi}{(1-2ik\xi)^2} + g_3' \oint_{\xi} \frac{H(\xi)d\xi}{(1+2ik\xi)^3} + g_{-3}' \oint_{\xi} \frac{H(\xi)d\xi}{(1-2ik\xi)^3}.
\end{aligned}$$

[ $H(\xi) \equiv \exp(-2qk\xi)F(\xi)$ ]

Since  $(1+2ik\xi) = \frac{2i}{n} (\xi - \frac{1}{2}in')$  and  $(1-2ik\xi) = -\frac{2i}{n} (\xi + \frac{1}{2}in')$ , we get two types of contour integrals in the complex  $\xi$ -plane.

1st type : Branch points at  $\xi = \pm \frac{1}{2}$ , Pole at  $\xi = +\frac{1}{2}in'$ .

2nd type: Branch points at  $\xi = \pm \frac{1}{2}$ , Pole at  $\xi = -\frac{1}{2}in'$ .

In the following list of values for the above integrals, the final results have been obtained by using Cauchy's theorem involving calculations of residues, viz. :

$$f(z) = \frac{1}{2\pi i} \oint_{\xi} \frac{f(\xi)d\xi}{(\xi-z)}, \quad f'(z) = \frac{1}{2\pi i} \oint_{\xi} \frac{f(\xi)d\xi}{(\xi-z)^2},$$

$$f''(z) = \frac{2}{2\pi i} \oint_{\xi} \frac{f(\xi)d\xi}{(\xi-z)^3}, \dots \quad f^n(z) = \frac{n!}{2\pi i} \oint_{\xi} \frac{f(\xi)d\xi}{(\xi-z)^{n+1}}.$$

$$(1) \quad \oint_{\xi} \frac{F(\xi)d\xi}{(1+2ik\xi)} = -\frac{4\pi n'}{(1+n'^2)} \exp(-2n' \cot^{-1} n');$$

$$(2) \quad \oint_{\xi} \frac{F(\xi)d\xi}{(1-2ik\xi)} = \frac{4\pi n'}{(1+n'^2)} \exp(2n' \cot^{-1} n');$$

$$(3) \quad \oint_{\xi} \frac{F(\xi)d\xi}{(1+2ik\xi)^2} = 0;$$

$$(4) \quad \oint_{\xi} \frac{F(\xi)d\xi}{(1-2ik\xi)^2} = \frac{16\pi n'^3}{(1+n'^2)^2} \exp(2n' \cot^{-1} n');$$

$$(5) \quad \oint_{\xi} \frac{F(\xi)d\xi}{(1+2ik\xi)^3} = \frac{4\pi n'^3}{(1+n'^2)^2} \exp(-2n' \cot^{-1} n');$$

$$(6) \quad \oint_{\xi} \frac{F(\xi)d\xi}{(1-2ik\xi)^3} = \frac{4\pi n'^3(11n'^2-1)}{(1+n'^2)^3} \exp(2n' \cot^{-1} n');$$

$$(7) \quad \oint_{\xi} \frac{H(\xi)d\xi}{(1+2ik\xi)} = \frac{-4\pi n'}{(1+n'^2)} \exp(q-2n' \cot^{-1} n');$$

$$(8) \quad \oint_{\xi} \frac{H(\xi)d\xi}{(1-2ik\xi)} = \frac{4\pi n'}{(1+n'^2)} \exp(-q+2n' \cot^{-1} n');$$

$$(9) \quad \oint_{\xi} \frac{H(\xi)d\xi}{(1+2ik\xi)^2} = \frac{4\pi n'q}{(1+n'^2)} \exp(q-2n' \cot^{-1} n');$$

$$(10) \quad \oint_{\xi} \frac{H(\xi)d\xi}{(1-2ik\xi)^2} = \left( \frac{4\pi n'q}{(1+n'^2)} + \frac{16\pi n'^3}{(1+n'^2)^2} \right) \exp(-q+2n' \cot^{-1} n');$$

$$(11) \quad \oint_{\xi} \frac{H(\xi)d\xi}{(1+2ik\xi)^3} = \left( \frac{4\pi n'^3}{(1+n'^2)^2} - \frac{2\pi n'q^2}{(1+n'^2)} \right) \exp(q-2n' \cot^{-1} n);$$



$$(12) \oint_{\xi} \frac{H(\xi) d\xi}{(1-2ik\xi)^3} = \left( \frac{4\pi n'^3(11n'^2-1)}{(1+n'^2)^3} + \frac{2\pi n'q^2}{(1+n'^2)} + \frac{16\pi n'^3q}{(1+n'^2)^2} \right) \times \\ \times \exp(-q+2n'\cot^{-1}n').$$

Substituting these calculated values of the contour integrals the value of  $J$  splits up into two component parts:—

$$J = \exp(2n'\cot^{-1}n') \{K\} + \exp(-2n'\cot^{-1}n') \{K^*\},$$

where

$$\{K\} = g_{-1} \cdot \frac{4\pi n'}{(1+n'^2)} + g_{-2} \cdot \frac{16\pi n'^3}{(1+n'^2)^2} + g_{-3} \cdot \frac{4\pi n'^3(11n'^2-1)}{(1+n'^2)^3} \\ + g'_{-1} \cdot \frac{4\pi n'\epsilon^{-q}}{(1+n'^2)} + g'_{-2} \cdot \left( \frac{16\pi n'^3\epsilon^{-q}}{(1+n'^2)^2} + \frac{4\pi n'q\epsilon^{-q}}{(1+n'^2)} \right) \\ + g'_{-3} \cdot \left( \frac{4\pi n'^3(11n'^2-1)\epsilon^{-q}}{(1+n'^2)^3} + \frac{16\pi n'^3q\epsilon^{-q}}{(1+n'^2)^2} + \frac{2\pi n'q^2\epsilon^{-q}}{(1+n'^2)} \right); \\ \{K^*\} = g_1 \cdot \left( \frac{-4\pi n'}{(1+n'^2)} \right) + g_3 \cdot \frac{4\pi n'^3}{(1+n'^2)^2} + g_1' \cdot \left( -\frac{4\pi n'\epsilon^q}{(1+n'^2)} \right) \\ + g_2' \cdot \frac{4\pi n'q\epsilon^q}{(1+n'^2)} + g_3' \cdot \left( \frac{4\pi n'^3\epsilon^q}{(1+n'^2)^2} - \frac{2\pi n'q^2\epsilon^q}{(1+n'^2)} \right).$$

The value of  $K$  is found to be zero after simplification, and that of  $K^*$

$$= \frac{4\pi n'G_1(q)}{(1+n'^2)} + \frac{4\pi n'^3G_2(q)}{(1+n'^2)^2};$$

where  $G_1(q) = (8/q^2 + 48/q^4) \cosh q - (24/q^3 + 48/q^5) \sinh q$ ,

$$G_2(q) = -32 \cosh q/q^4 + 32 \sinh q/q^5.$$

Hence the value of

$$J = e^{-2n'\cot^{-1}n'} \cdot \left[ \frac{4\pi n'}{(1+n'^2)} G_1(q) + \frac{4\pi n'^3}{(1+n'^2)^2} G_2(q) \right].$$

## APPENDIX.

## TABLE IV.

$\nu$	$\text{Exp} \left[ -2\pi \sqrt{\nu_0/(\nu-\nu_0)} \right]$	$\text{Cot}^{-1} \left[ \sqrt{\nu_0/(\nu-\nu_0)} \right]$
$1\nu_0$	0·00000	0·0000
$2\nu_0$	0·00184	0·7854
$3\nu_0$	0·01180	0·9554
$4\nu_0$	0·02678	1·0475
$5\nu_0$	0·04328	1·1071
$6\nu_0$	0·06020	1·1504
$7\nu_0$	0·07330	1·1834
$8\nu_0$	0·09348	1·2094
$9\nu_0$	0·10861	1·2310
$10\nu_0$	0·13810	1·2490
$11\nu_0$	0·15260	1·2646

TABLE V.

$$\text{Values of } L = \exp \left[ -4\sqrt{\nu_0/(\nu-\nu_0)} \cdot \cot^{-1} \sqrt{\nu_0/(\nu-\nu_0)} \right].$$

(When  $\nu = \nu_0$ ,  $L = \epsilon^{-4} = 0.0183$ .)

$\nu = 2\nu_0$	$L = 0.0433$	$\nu = 7\nu_0$	$L = 0.1449$
$= 3\nu_0$	$= 0.0670$	$= 8\nu_0$	$= 0.1601$
$= 4\nu_0$	$= 0.0890$	$= 9\nu_0$	$= 0.1753$
$= 5\nu_0$	$= 0.1093$	$= 10\nu_0$	$= 0.1892$
$= 6\nu_0$	$= 0.1278$	$= 11\nu_0$	$= 0.2021$

TABLE VI.

$$X^2 = (2.514) (\nu_0/\nu)^2 \exp(-4n' \cot^{-1} n') / (1 - \exp(-2\pi n')).$$

(When  $\nu = \nu_0$ ,  $X^2 = 2.5140 \epsilon^{-4} = 0.0461$ .)

$\nu = 2\nu_0$	$X^2 = 0.0272$	$\nu = 7\nu_0$	$X^2 = 0.0080$
$= 3\nu_0$	$= 0.0189$	$= 8\nu_0$	$= 0.0069$
$= 4\nu_0$	$= 0.0143$	$= 9\nu_0$	$= 0.0060$
$= 5\nu_0$	$= 0.0114$	$= 10\nu_0$	$= 0.0055$
$= 6\nu_0$	$= 0.0095$	$= 11\nu_0$	$= 0.0051$

TABLE VII.

$$F(X, S) = S^2/(1+S^2)(1+X^2-S).*$$

(When  $\nu = \nu_0$ ,  $F(X, S) = 1.2330$ .)

$\nu = 2\nu_0$	$F(X, S) = 1.3150$	$\nu = 7\nu_0$	$F(X, S) = 1.4134$
$= 3\nu_0$	$= 1.3552$	$= 8\nu_0$	$= 1.4195$
$= 4\nu_0$	$= 1.3791$	$= 9\nu_0$	$= 1.4246$
$= 5\nu_0$	$= 1.3968$	$= 10\nu_0$	$= 1.4271$
$= 6\nu_0$	$= 1.4050$	$= 11\nu_0$	$= 1.4297$

\* We must remember that  $S$  has the value 0.7543 and  $S^2$  the value 0.5619 when  $q$  has the value 1.418 in Hartree units.

TABLE VIII.

$$F^*(X, S) = S^2/(1-S^2) (1-X^2+S).$$

$$(\text{When } \nu = \nu_0, F^*(X, S) = 0.7509.)$$

$\nu = 2\nu_0$	$F^*(X, S) = 0.7426$	$\nu = 7\nu_0$	$F^*(X, S) = 0.7344$
$= 3\nu_0$	$= 0.7390$	$= 8\nu_0$	$= 0.7339$
$= 4\nu_0$	$= 0.7370$	$= 9\nu_0$	$= 0.7335$
$= 5\nu_0$	$= 0.7358$	$= 10\nu_0$	$= 0.7333$
$= 6\nu_0$	$= 0.7350$	$= 11\nu_0$	$= 0.7332$

TABLE IX.

$$\Phi(\nu) = 0.7770(\nu_0/\nu) - 2.2038 (\nu_0/\nu)^2.$$

$\nu$	$\Phi(\nu)$	$[\Phi(\nu)]^2$
$1\nu_0$	-1.4268	2.035758
$2\nu_0$	-0.1624	0.026374
$3\nu_0$	0.0141	0.000199
$4\nu_0$	0.0565	0.003192
$5\nu_0$	0.0673	0.004529
$6\nu_0$	0.0683	0.004665
$7\nu_0$	0.0661	0.004369
$8\nu_0$	0.0627	0.003931
$9\nu_0$	0.0591	0.003493
$10\nu_0$	0.0557	0.003102
$11\nu_0$	0.0524	0.002746

Before proceeding to prepare a table for the absorption coefficient we should remember that according to our scheme of notation

$$\tau_{\nu}^{+}(e) = \frac{8\pi^3\nu e^2}{c} L(\nu)F(X, S) \Phi^2(\nu);$$

$$\tau_{\nu}^{-}(e) = \frac{8\pi^3\nu e^2}{c} L(\nu)F^*(X, S) \Phi^2(\nu);$$

and the values of the several factors have already been computed in the foregoing tables. In the adjoining table X are attached the values of  $\tau_{\nu}^{+}(e)$  and  $\tau_{\nu}^{-}(e)$  when these are each divided by  $8\pi^3\nu_0 e^2/c$ .

TABLE X.

$\nu$	$L(\nu)\Phi^2(\nu)$	$\tau_{\nu}^{+}(e)/\frac{8\pi^3\nu_0e^2}{c}$	$\tau_{\nu}^{-}(e)/\frac{8\pi^3\nu_0e^2}{c}$
$1\nu_0$	$3.7255 \times 10^{-2}$	$459.35 \times 10^{-4}$	$279.75 \times 10^{-4}$
$2\nu_0$	$0.1143 \times 10^{-2}$	$30.06 \times 10^{-4}$	$16.98 \times 10^{-4}$
$3\nu_0$	$0.0013 \times 10^{-2}$	$0.52 \times 10^{-4}$	$0.28 \times 10^{-4}$
$4\nu_0$	$0.0028 \times 10^{-2}$	$1.56 \times 10^{-4}$	$0.83 \times 10^{-4}$
$5\nu_0$	$0.0495 \times 10^{-2}$	$34.57 \times 10^{-4}$	$18.21 \times 10^{-4}$
$6\nu_0$	$0.0596 \times 10^{-2}$	$50.24 \times 10^{-4}$	$26.28 \times 10^{-4}$
$7\nu_0$	$0.0633 \times 10^{-2}$	$62.62 \times 10^{-4}$	$32.54 \times 10^{-4}$
$8\nu_0$	$0.0629 \times 10^{-2}$	$71.43 \times 10^{-4}$	$36.93 \times 10^{-4}$
$9\nu_0$	$0.0612 \times 10^{-2}$	$78.47 \times 10^{-4}$	$40.40 \times 10^{-4}$
$10\nu_0$	$0.0586 \times 10^{-2}$	$83.63 \times 10^{-4}$	$42.97 \times 10^{-4}$
$11\nu_0$	$0.0555 \times 10^{-2}$	$87.28 \times 10^{-4}$	$40.69 \times 10^{-4}$

TABLE XI.

$\nu$	$\Phi(\nu)$	$[\Phi(\nu)]^2$	$\tau_{\nu}^{+} / \frac{8\pi^3\nu_0e^2}{c} L(\nu)F(X, S)$ = $T(\nu)$ = $\tau_{\nu}^{-} / \frac{8\pi^3\nu_0e^2}{c} L(\nu)F^*(X, S)$	REMARKS
$\nu_0$	-1.4268	2.0358	$6.2717 \times 10^{-2}$	Corresponding to the value of $M_{kk'}^{\nu}$ ( $V'' = 0, V' = 0$ ), viz., $3.0807 \times 10^{-2}$ .
$\nu_0 + \frac{1}{4}\omega_0'$	-1.4110	1.9909	$6.1334 \times 10^{-2}$	
$\nu_0 + \frac{1}{2}\omega_0'$	1.3952	1.9466	$5.9969 \times 10^{-2}$	
$\nu_0 + \frac{3}{4}\omega_0'$	1.3798	1.9038	$5.8650 \times 10^{-2}$	
$\nu_0 + \omega_0'$	1.3640	1.8605	$16.7858 \times 10^{-2}$	Corresponding to the value of $M_{kk'}^{\nu}$ ( $V'' = 0, V' = 1$ ), viz., $9.0222 \times 10^{-2}$ .
$\nu_0 + \frac{5}{4}\omega_0'$	1.3496	1.8214	$16.4330 \times 10^{-2}$	
$\nu_0 + \frac{3}{2}\omega_0'$	1.3349	1.7819	$16.0767 \times 10^{-2}$	
$\nu_0 + \frac{7}{4}\omega_0'$	1.3203	1.7432	$15.7275 \times 10^{-2}$	

$\nu$	$\Phi(\nu)$	$[\Phi(\nu)]^2$	$\tau_\nu^+ \left/ \frac{8\pi^2\nu_0 e^2}{c} L(\nu)F(X, S) \right.$ $= T(\nu) =$ $\tau_\nu^- \left/ \frac{8\pi^2\nu_0 e^2}{c} L(\nu)F^*(X, S) \right.$	REMARKS
$\nu_0 + 2\omega_0'$	1.3045	1.7017	$17.7120 \times 10^{-2}$	Corresponding to the value of $M_{kk'}^{\nu}$ ( $V'' = 0, V' = 2$ ), viz., $10.4084 \times 10^{-2}$ .
$\nu_0 + \frac{3}{2}\omega_0'$	1.2916	1.6682	$17.3133 \times 10^{-2}$	
$\nu_0 + \frac{5}{2}\omega_0'$	1.2780	1.6333	$17.0000 \times 10^{-2}$	
$\nu_0 + \frac{11}{4}\omega_0'$	1.2640	1.5977	$16.6295 \times 10^{-2}$	Corresponding to the value of $M_{kk'}^{\nu}$ ( $V'' = 0, V' = 3$ ), viz., $5.8303 \times 10^{-2}$ .
$\nu_0 + 3\omega_0'$	1.2435	1.5588	$9.0883 \times 10^{-2}$	
$\nu_0 + \frac{13}{4}\omega_0'$	1.2368	1.5297	$8.9186 \times 10^{-2}$	
$\nu_0 + \frac{7}{2}\omega_0'$	1.2237	1.4974	$8.7303 \times 10^{-2}$	Corresponding to the value of $M_{kk'}^{\nu}$ ( $V'' = 0, V' = 4$ ), viz., $1.4116 \times 10^{-2}$ .
$\nu_0 + \frac{15}{4}\omega_0'$	1.2106	1.4656	$8.5449 \times 10^{-2}$	
$\nu_0 + 4\omega_0'$	1.1945	1.4268	$2.0141 \times 10^{-2}$	
$\nu_0 + \frac{17}{4}\omega_0'$	1.1848	1.4038	$1.9816 \times 10^{-2}$	Corresponding to the value of $M_{kk'}^{\nu}$ ( $V'' = 0, V' = 4$ ), viz., $1.4116 \times 10^{-2}$ .
$\nu_0 + \frac{9}{2}\omega_0'$	1.1722	1.3741	$1.9397 \times 10^{-2}$	
$\nu_0 + \frac{19}{4}\omega_0'$	1.1597	1.3449	$1.8985 \times 10^{-2}$	
$\nu_0 + 5\omega_0'$	1.1448	1.3106	$0.0709 \times 10^{-2}$	$M_{kk'}^{\nu}$ ( $V'' = 0, V' = 5$ ) = $0.0541 \times 10^{-2}$ .
$\nu_0 + 6\omega_0'$	1.0960	1.2012	$0.0400 \times 10^{-2}$	$M_{kk'}^{\nu}$ ( $V'' = 0, V' = 6$ ) = $0.0333 \times 10^{-2}$ .

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