1946

The determination of molecular hydrogen spectrum between 5200 and 5800

BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

THE DETERMINATION OF MOLECULAR HYDROGEN SPECTRUM BETWEEN λ5200 AND λ5800

by

Grace Rosalie White

(B.S., Eastern Nazarene College, 1946)

submitted in partial fulfilment of the

requirements for the degree of

Master of Arts

1946

Approved

by

First Reader Lucien B. Taylor

Professor of Physics

Second Reader

Professor of Physics

OUTLINE OF THE THESIS

INTRODUCTION

Hydrogen is the simplest atomic structure in nature. The hydrogen atom is made up of one electron and one proton; the hydrogen molecule, two electrons and two protons. Bohr used the hydrogen model to build up the structure of all chemical atoms. The atomic hydrogen spectrum has consequently been carefully studied and its wave numbers accurately determined. On the other hand the molecular hydrogen spectrum was one of the first cases on which the old classical quantum mechanics broke down. It is a complicated spectrum as compared with the atomic hydrogen spectrum and many of its wave lengths are not known with certainty.

In this paper an attempt has been made to present pertinent parts of the theory of the structure of atomic hydrogen, a detailed and mathematical theoretical study of the hydrogen molecular spectrum, and experimental data on molecular hydrogen spectrum between $\lambda 5200$ and $\lambda 5800$.

ATOMIC SPECTRA

The Bohr Theory

According to classical electrodynamics, the atom should radiate energy continuously at a rate proportional to the square of the acceleration of the electron. In this case there would be a continuous variation in the total energy, E, and hence the radiation would consist of a continuous spectrum. To explain the observed sharp line spectrum of atomic hydrogen Bohr postulated that only those orbits are permissible for which the angular momentum of the electron is a whole multiple of $h/2\pi$. These stationary orbits may be expressed as $mvr = nh/2\pi$ (1) where n is an integer and mvr is equal to the angular momentum of the electron. According to Bohr, radiation does not take place while an electron moves in its orbit, but only when the electron goes from one level of energy to another level of energy. The quantum of light emitted may be expressed as $h\nu' = hc\nu = E_1 - E_2$ (2) where ν' is the frequency, ν is the wave number of light, c is the velocity of light (2.9978×10^{10} cm/sec.), h is Planck's constant (6.610×10^{-27} erg sec.), and the E's are energy levels with subscripts indicating the shells. The Bohr frequency condition also holds for the absorption of light and hence the wave number of absorbed or emitted light may be expressed as

$$\nu = \frac{E_1}{hc} - \frac{E_2}{hc} \qquad (3)$$

Substituting the energy values of the hydrogen atom into the

equation gives $\nu = RZ^2(\frac{1}{n_2^2} - \frac{1}{n_1^2})$ where n_1 and n_2 are (4)
principal quantum numbers of the two states concerned, Z is the atomic number, and $R = R'/hc = 2\pi^2 e^4/ch^3 = 109{,}677.76\ cm^{-1}$ = Rydberg constant. Equation (4) gives an accurate expression of the whole spectrum of the hydrogen atom. Thus we see that the wave number of a spectral line can be represented as the difference between two terms.

From Coulomb's law the force of attraction between the nucleus and the electron can be expressed as

$$F = \frac{Ee}{r^2} = \frac{-e^2}{kr^2} \qquad (5)$$

where E is the charge on the nucleus and e, the charge on the electron. From Newton's second law of motion

$$F = ma = \frac{mv^2}{kr} \qquad (6)$$

where m equals the mass of the electron, a the centripetal acceleration, and v, the velocity of the electron. Equating (5) and (6) and rearranging terms gives $mv^2 = e^2/kr$. (7)
Eliminating v from (1) and (7) and solving for r gives the permissible orbits.

Corrections

Sommerfeld introduced three refinements to the Bohr theory. In Bohr's equation $r = \frac{n^2h^2}{4\pi^2me^2Z}$ where m is the mass of the electron, r gives the radii of the possible orbits. Sommerfeld found it necessary to replace m by the reduced mass $= \frac{mM}{m+M}$ since the electron as well as the nucleus revolves about the common center of gravity rather

than the nucleus.

Sommerfeld replaced circular orbits by elliptic orbits. In an ellipse r is not constant and hence must be considered along with the angle of rotation ϕ. The action integrals

$$\oint p_\varphi d\varphi = n_\varphi h/2\pi \qquad \text{and} \qquad \oint p_r \, dr = n_r \, h/2\pi$$

where n_φ is the azimuthal quantum number and n_r is the radial quantum number express the angular and radial momentum as integral multiples of $h/2\pi$. The azimuthal quantum number is a measure of the minor axis of the ellipse and the principal quantum number n is a measure of the major axis.

Sommerfeld also found that the axis of the ellipse rotates slowly and uniformly about the center of gravity. Thus he applied relativistic mechanics to the motion of the electron.

The energy of the elliptic orbit

$$E_{n_r, n_\varphi} = - \frac{2m' e^4 Z^2}{\hbar^2 n^2} \left[1 + \frac{e^4 Z^2}{\hbar^2 c^2 n^2} \left(\frac{1}{n} - \frac{3}{4n_r} \right) \right.$$

where $\hbar = h/2\pi$ varies only slightly for a given value of r from that of the circular orbit. The variation is due to a relativistic correction depending on n_φ. The latter quantum number also forms a basis for the explanation of some of the fine structure of the lines.

Uhlenbeck and Goudsmit introduced an electron spin to account for the fine structure of lines in spectral series of some of the elements and anomalous Zeeman effect.

Different forms of coupling are possible when there are several electrons in one atom. In the Russell-Saunders

coupling, the l values for all the electrons are added vectorially giving the vector L. The vectorial sum of the spin vectors for each electron gives the vector S. The vectorial addition of L and S gives the vector J. In the jj coupling individual l and s vectors add to give j, and the j vectors for all electrons are added.

Pauli's exclusion principle, forbidding the existence in one atom of two electrons with the same quantum numbers, was used to determine the number and properties of all the electrons in a given atom.

In general in allowed transitions, $\Delta L = \pm 1$ and $\Delta J = \pm 1$ or 0, but not $J = 0 \rightarrow J = 0$.

Breakdown of the Bohr Theory

The Bohr theory of the electron worked very well for the hydrogen atom upon which it was based, but broke down when applied to the more complex atoms and molecules. The ionization potential is the voltage necessary to supply just enough energy to ionize the hydrogen atom, that is, to remove the electron from the lowest orbit of hydrogen, $n = 1$, to $n = \infty$, outside the atom. The numerical value of this potential can be computed from the values of the two energy levels E_∞ and E_1. Comparable values for the theoretical and experimental ionization potentials of the hydrogen atom were obtained. Because of the simplicity of the structure of molecular hydrogen, the value of its ionization potential could be calculated on the basis of the old quantum mechanics.

The experimental value was expected to be a few tenths higher than the value calculated theoretically because some vibrational levels generally become excited when a molecule is ionized by an electron impact. Theoretically the potential for molecular hydrogen was calculated at 23.7 volts. Experimentally it was determined to be 15.9 volts. This discrepancy marked the breakdown of the old theory as applied to the molecular spectrum of hydrogen.

MOLECULAR SPECTRA

Molecular Hydrogen, H_2

The breakdown of the simpler Bohr theory necessitated a new and more complicated theory which would be in agreement with experimental data. Several persons worked out a new quantum mechanics, each by a different method. Dirac used symbols; Heisenberg, matrices; and Schroedinger, differential equations.

Neglecting relativity and electron and nuclear spin, the new quantum mechanics may be expressed by Schroedinger's wave equation. For the hydrogen molecule, consisting of two nuclei and two electrons, this equation in Cartesian co-ordinates is

$$\frac{h^2}{8\pi^2}\left\{\frac{1}{M_a}\nabla_a^2\psi + \frac{1}{M_b}\nabla_b^2\psi + \frac{1}{m_1}\nabla_1^2\psi + \frac{1}{m_2}\nabla_2^2\psi\right\}$$

$$\left\{\frac{E_a e_1}{r_{a1}} + \frac{E_b e_1}{r_{b1}} + \frac{E_a e_2}{r_{a2}} + \frac{E_b e_2}{r_{b2}} - \frac{E_a E_b}{r_{ab}} - \frac{e_1 e_2}{r_{12}} + E\right\}\psi = 0 \qquad (8)$$

which is a relationship among masses, radii, and energies. The M's are nuclei masses, the m's are electron masses, the E's with subscripts are charges on the nuclei, the e's are charges on the electrons, and the E is the energy. Since $\frac{m}{M_a}$ and $\frac{m}{M_b}$ are both small quantities, as a first approximation the first two terms may be omitted and the equation becomes

$$\frac{h^2}{8\pi^2 m}\left\{\nabla_1^2\psi + \nabla_2^2\psi\right\} + \left\{\frac{E_a e_1}{r_{a1}} + \frac{E_b e_1}{r_{b1}} + \frac{E_a e_2}{r_{a2}} + \frac{E_b e_2}{r_{b2}} - \frac{e_1 e_2}{r_{12}} + E\right\}\psi = 0 \qquad (9)$$

The solution of Schroedinger's equation gives the probability of the location of an electron as a function of co-ordinate position. Letting $E_2 = E_1 - \frac{E_a E_b}{r_{ab}}$ fixes the nculei at a certain distance from one another and hence eliminates (1) the possibility of vibration of the nuclei in the direction of the internuclear axis r_{ab} and (2) the rotation of the axis about some other axis.

If ψ (v) is a wave function involving only the vibrational quantum number v, ψ(R) is another involving only the rotational quantum number R, and ψ(8) is a solution of (8), then $\psi(8) = \psi(9)\psi(v)\psi(R)$ (10)
is the form taken by solutions ψ(9) of (9) to the approximation considered. $\psi(v) = e^{-\frac{\omega_e \rho^2}{4B_e}} H(\rho)$ when (11)

$U(\rho) = E_{e_1} + b_2\rho^2$ where the latter is a useful approximation for only small vibrational values of ρ and is only applicable to small vibrational quantum numbers and rather heavy molecules. Here ρ is defined by $r = r_e(1+\rho)$; r_e is the equilibrium value of the internuclear distance; E_{e1} denotes the value of the energy in the equilibrium configuration, and b_2 is a constant. The wave functions (11) depend on the form taken for the potential energy (12) of the nuclei. $E_v = hc\omega_e(v+\frac{1}{2})$ is the first term of a series of powers of v representing the vibrational wave functions in the case of H_2 where ρ is not small. (12)

In order to obtain the wave functions (11) the Hermitic

polynomial $H(\rho) = \sum_v a_v \rho^v$ must be determined. It has its (13)
coefficients a_v determined by the recursion formula

$$(v+1)(v+2)a_{v+2} = a_v \left[\frac{\omega_e(2v+1)}{2B_e} - \frac{E_v}{hcB_e} \right] . \qquad (14)$$

The constants ω_e, the fundamental vibration frequency in the equilibrium configuration, and the constant Be, which corresponds to the equilibrium separation r_e, are given by

$$\frac{b_2}{2\pi^2 I_e} = \omega_e{}^2 c^2 \quad (15) \qquad \text{and} \qquad \frac{h}{8\pi^2 I_e} = cB_e \qquad (16)$$

where c is the velocity of light and I_e, the moment of inertia of the molecule about an axis perpendicular to the line joining the nuclei.

In polar co-ordinates where r is constant $\psi(R)$ becomes

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left[\sin\theta \frac{\partial\psi}{\partial\theta} \right] + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\varphi^2} + \frac{E_{rot}}{hcB_e}\psi = 0 \qquad (17)$$

which is the equation of the zonal surface harmonic. Since it has finite solutions only when $E_{rot}/hcB_e = K(K+1)$ where K is a positive integer, the proper rotational energy values $E_{rot} = hcB_e\, K(K+1)$, K = 0,1,2,3, etc. The solutions (18)
of (17) corresponding to each K can be any one of the 2K+1 functions

$$\cos(M\varphi)\sin^M\theta \frac{d^M}{(d\cos\theta)^M} P_K(\cos\theta), \quad M = 0,1,2\ldots K$$

$$\sin(M\varphi)\sin^M\theta \frac{d^M}{(d\cos\theta)^M} P_K(\cos\theta), \quad M = 1,2,\ldots K \qquad (19)$$

or any linear combination of them. There is a consequent $2K+1$ fold degeneracy and any rotational state with quantum number K has a statistical weight $2K+1$. In terms of Schroedinger's theory an eigenvalue is degenerate when a given operator has more than one eigenvalue for one eigenfunction, e.g. if $\alpha u = \lambda u$ and $\alpha v = \lambda v$, λ is degenerate. The total number of nodes is K, for each of the functions (19) has M plane nodes φ is a constant and K - M conical nodes θ, constant. The zonal harmonics, $P_K(\cos\theta)$, in (19) are $P_0(\cos\theta) = 1$; $P_1(\cos\theta) = \cos\theta$; $P_2(\cos\theta) = 3/2\cos^2\theta - \frac{1}{2}$; $P_3(\cos\theta) = 5/2\cos^3\theta - 3/2\cos\theta$; etc.

The Hydrogen Molecular Ion, H_2^+

It is impossible to visualize the wave functions which solve (9), the simplest form of the wave equation containing the essentials for H_2, because they occupy six-dimensional space. There are three space co-ordinates for each of the two electrons and it is therefore easier to grasp the meaning of the molecular spectroscopic quantum numbers if the binuclear one electron system, H_2^+, is studied. Removing the terms in (9) involving the second electron gives

$$\frac{h^2}{8\pi^2 m}\nabla^2\psi + \left\{\frac{e^2}{r_1} + \frac{e^2}{r_2} + E\right\}\psi = 0 \qquad (20)$$

where r_1 and r_2 are the distances from the electron to each

of the two protons and $E_a = E_b = e$ numerically for H_2^+.

The solutions of wave equations such as (9) or (20) must be finite, continuous, and single-valued in the space of the particle or electron and must satisfy appropriate conditions at the boundary. Therefore solutions will only exist for proper values of E which may form either a discrete or continuous set of numbers extending between certain limits or may be interpreted geometrically, but physical interpretation is possible only when the ψ-function is multiplied by its conjugate function ψ^* and a volume element dv. $\psi\psi^* dv$ represents the probability that the electron will be found in the volume dv at a given instant. ψ is normalized when the units are so adjusted that the whole distribution $\iiint \psi\psi^* dv$ represents one electron.

If ψ_m and ψ_n are two solutions of the same wave equation with proper values E_m and E_n, then

$$\iiint \psi_m \psi_n \, dv = 0 ; \qquad (21)$$

$m \neq n$ unless the system is degenerate. The set of functions $\psi_1\psi_2 \ldots\ldots \psi_m\psi_n$ satisfying the equation are said to be orthogonal. If x is a co-ordinate of the electron, $\iiint ex\psi\psi^* dv$ should be the x component of the contribution to the dipole moment of the molecule which arises from the electron. Therefore a knowledge of ψ should tell something about the

dipole moments of the molecules and that behaviour that will make possible a determination of the intensity of the radiation they emit. ψ should give (1) the average distribution of the electron in space (2) proper values of energy which are directly related to the frequency of the spectral lines and (3) data concerning electron moments that will provide information for determination of intensities of spectral lines where zero intensities indicate transitions are forbidden.

Equation (20) is separable in the ellipsoidal co-ordinate $= \frac{r_a + r_b}{r}$, the hyperboloidal co-ordinate $= \frac{r_a - r_b}{r}$, and the planes through the internuclear axis, giving the angle of revolution . The partial differential equation thus formed can be broken up into three ordinary differential equations:

$$\frac{1}{\psi(\varphi)} \frac{d^2\psi(\varphi)}{d\varphi^2} + \alpha = 0 \tag{22}$$

$$\frac{1}{\psi(\xi)}\left[(\xi^2 - 1)\frac{d^2\psi(\xi)}{d\xi^2} + 2\xi\frac{d\psi(\xi)}{d\xi}\right] - \frac{\alpha}{\xi^2 - 1} + \frac{2\pi^2 mr^2}{h^2}\left[\frac{(E_a + E_b)e\xi}{r} + E\xi^2\right] = \beta \tag{23}$$

$$\frac{1}{\psi(\eta)}\left[(1-\eta^2)\frac{d^2\psi(\eta)}{d\eta^2} - 2\eta\frac{d\psi(\eta)}{d}\right. - \frac{\alpha}{1-\eta^2} + \frac{2\pi^2 mr^2}{h^2}\left[\frac{(E_a - E_b)e\eta}{r} - E\eta^2\right] = -\beta \tag{24}$$

The ψ's solving these equations must have all the properties heretofore discussed. If the angle φ is single valued, $\psi(\varphi + 2k\pi) = \psi(\varphi)$ where k is any integer. (25)

With A's and B's as undetermined constants

$\psi(\varphi) = A_1 e^{i\sqrt{\alpha}\varphi} + A_2 e^{-i\sqrt{\alpha}\varphi}$ (26) or $= B_1 \cos\sqrt{\alpha}\varphi + B_2 \sin\sqrt{\alpha}\varphi$ (27)

become the solutions of (22). Because of (25) and (26)

has to satisfy the infinite set of equations

$$
\begin{aligned}
&A_1 e^{i\sqrt{\alpha}\varphi}(1-e^{2\pi i\sqrt{\alpha}}) + A_2 e^{-i\sqrt{\alpha}\varphi}(1 - e^{-2\pi i\sqrt{\alpha}}) = 0 \\
&A_1 e^{i\sqrt{\alpha}\varphi}(1-e^{4\pi i\sqrt{\alpha}}) + A_2 e^{-i\sqrt{\alpha}\varphi}(1 - e^{-4\pi i\sqrt{\alpha}}) = 0 \qquad (28) \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
&A_1 e^{i\sqrt{\alpha}\varphi}(1 - e^{2\pi k i\sqrt{\alpha}}) + A_2 e^{-i\sqrt{\alpha}\varphi}(1 - e^{-2\pi k i\sqrt{\alpha}}) = 0 \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots
\end{aligned}
$$

if $e^{2\pi i\sqrt{\alpha}} = 1 = e^{-2\pi i\sqrt{\alpha}}$ or $\alpha = \lambda^2$, $\lambda = 0,1,2,$etc.

When $\lambda = 0$, $\psi(\varphi)$ is a constant; for other values, an infinite number of functions satisfy all the conditions to which the wave function $\psi(\varphi)$ is subject. But these are all linear combinations of any two that are mutually independent so that there are really only two independent wave functions for each value of λ $(\lambda > 0)$. There is a two-fold degeneracy understandable from the fact that nothing is said about the fixation of a plane from which φ is to be measured. If the nuclei are allowed to rotate so that they prescribe a direction perpendicular to the internuclear axis, degeneracy will be removed and each of the "levels" determined by λ $(\lambda > 0)$ become doubled.

Equations (23) and (24) possess wave-functions which satisfy the conditions of integrability for discrete sets of values of the separation constant β and of the energy E. If the infinite set of discrete values β_λ, for β for which (23) and (24) have a solution satisfying the conditions,

are arranged in order, there will be an infinite series $E_{\xi\lambda}$ of E for which a wave function exists. States with $\lambda = 0$ have a statistical weight one and one wave function for each proper value of $E_{\xi\lambda}$. States with $\lambda > 0$ have a statistical weight of two and two wave functions for every proper value of $E_{\xi\lambda}$.

Since ψ is a wave function separable into $\psi(\xi)\psi(\eta)\psi(\varphi)$, if $\psi = 0$, one of the associated ψ's must equal zero. The equation $\psi = 0$ represents a nodal surface in space and is called the nodal surface of the wave function. The nodal surfaces of the other functions, $\psi(\xi)$, $\psi(\eta)$, $\psi(\varphi)$ have already been defined respectively as ellipsoids, hyperboloids, and a set of planes passing through the internuclear axis. Keeping two wave functions fixed and arranging the other associated set in order of proper values of $E(\xi, \eta, \varphi)$ upward gives nodes of $\psi\varphi$ (associated set) as 0,1,2,etc. A quantum number for a term or level of the system, E, may therefore be defined as the number of nodes in the associated wave functions for one of the co-ordinates into which the wave equation is separable. In the domain $0 < \varphi < 2\pi$, $\psi(\varphi)$ has exactly λ nodes. The quantum number for φ is used to describe the state of the molecule; $\frac{\lambda h}{2\pi}$ is the angular momentum of the electron about the internuclear axis. Quantum numbers of the co-ordinates ξ and η are not used. Instead two combinations of the three primitive quantum numbers are used, l and n, which are analogous to the principal and azimuthal quantum

numbers of atomic spectroscopy. The ℓ is the sum of the nodes of $\psi(\varphi)$ and $\psi(\eta)$ and n = nodes of $\psi(\varphi)$ + nodes of $\psi(\eta)$ + nodes of $\psi(\xi)$ + 1. The condition $n - 1 \geq \ell \geq \lambda$ restricts n, ℓ, and λ. It is customary to express values of ℓ by a series of letters s,p,d,f,g,h,i,k,l... and values of λ by Greek small letters, each set of lettering being for values of the quantum numbers 0,1,2,3,4.....

Heitler and London Treatment

Heitler and London treated the molecules as made up of two neutral hydrogen atoms in their respective ground states to a first approximation and then considered how the wave functions of the atoms would have to be modified to satisfy Schroedinger's equation which applies when the nuclear distance is kept constant. The unperturbed wave functions are taken which imply that one electron is near one nucleus and the other electron is near the other nucleus. This can be expressed $\psi_1\varphi_2$ or $\psi_2\varphi_1$. If the first electron belongs to nucleus a, $\psi_1 = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} e^{-r_{a1}/a_o}$; to nucleus b, (29)

$$\varphi_1 = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} e^{-r_{b1}/a_o} . \qquad (29')$$

Both of these wave functions exist in x,y,z space but differ entirely because they are in different parts of the space. Corresponding terms for the second electron are

$$\psi_2 = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} e^{-r_{a2}/a_o} \quad \text{and} \quad \varphi_2 = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} e^{-r_{b2}/a_o} \qquad (30)$$

in x_2, y_2, z_2 space. In all cases a_o is the radius of the first Bohr orbit.

The two-fold degeneracy resulting from $\psi_1\varphi_2$ and $\psi_2\varphi_1$'s belonging to the same energy values of the unperturbed system, may be removed by taking two orthogonal linear combinations of them,

$$\alpha = a\psi_1\varphi_2 + b\psi_2\varphi_1$$
$$\beta = c\psi_1\varphi_2 + d\psi_2\varphi_1 \tag{31}$$

under the conditions

$$a^2 + b^2 + 2ab\,S = 1$$
$$c^2 + d^2 + 2cd\,S = 1$$
$$ac + bd + (ad + bc)S = 0 \tag{32}$$
$$S = \int \psi_1\varphi_1\psi_2\varphi_2\,dv_1dv_2$$

which normalize α and β and provide that they be orthogonal.

As a result of (32)

$$\alpha = \frac{1}{\sqrt{2 + 2S}}(\psi_1\varphi_2 + \psi_2\varphi_1)$$
$$= \frac{1}{\sqrt{2 - 2S}}(\psi_1\varphi_2 - \psi_2\varphi_1) \tag{33}$$

When values $v_\alpha = \chi_\alpha - \alpha$, $v_\beta = \chi_\beta - \beta$ are substituted in (9) (34)

$$E_\alpha = 2E_0 + E_{11} - \frac{E_{11}S - E_{12}}{1 + S} \quad \text{belonging to } \frac{\psi_1\varphi_2 + \psi_2\varphi_1}{\sqrt{2 + 2S}} \tag{35}$$

(sym. in 1 and 2)

and

$$E_\beta = 2E_0 + E_{11} + \frac{E_{11}S - E_{12}}{1 - S} \quad \text{belonging to } \frac{\psi_1\varphi_2 - \psi_2\varphi_1}{\sqrt{1^2 - 2S}} \tag{36}$$

(anti. in 1 and 2)

result. Here $E_0 = -Rhc$ = energy of ground state of hydrogen atom,

$$E_{11} = \int\left[\left(\frac{e^2}{r_{12}} + \frac{e^2}{r}\right)\frac{\psi_1^2\varphi_2^2 + \psi_2^2\varphi_1^2}{2} - \left(\frac{e^2}{r_{a1}} + \frac{e^2}{r_{b2}}\right)\frac{\psi_2^2\varphi_1^2}{2} - \left(\frac{e^2}{r_{a2}} + \frac{e^2}{r_{b1}}\right)\frac{\psi_1^2\varphi_2^2}{2}\right]dv_1dv_2 \tag{37}$$

$$E_{12} = \int\left(\frac{2e^2}{r_{12}} + \frac{2e^2}{r} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}}\right)\frac{\psi_1\varphi_1\psi_2\varphi_2}{2}\,dv_1dv_2 \tag{38}$$

The occurrence of two different energy values E_α and E_β is a result of the possibility of interchange of two electrons in the molecule. With the foregoing equations, however, such interchange would be probable only at atomic distances. $E_\beta > E_\alpha$ since the symmetric function $\frac{\psi_1\varphi_2 + \psi_2\varphi_1}{\sqrt{2 + 2S}}$ has no nodes and the antisymmetric function $\frac{\psi_1\varphi_2 - \psi_2\varphi_1}{\sqrt{2 - 2S}}$ has one node. E_β is always positive which means the atoms repel each other at all distances and hence a molecule with this type of wave function can not exist physically. E_α has a minimum at about $r = 3a_0/2$, which is the internuclear distance for the normal hydrogen molecule in the ground state. At greater distances the nuclei attract each other; at smaller, they repel. From a study of curves in which the energy of hydrogen molecules is graphed as a function of the internuclear distance, one sees that the formation of the molecule is due more particularly to the interlapping of the wave-functions which give rise to the electron interchange phenomena.

Electron Spin Effects

To explain the existence of multiplets, electrons have been assigned a quantized rotation or spin for which there are only two possible quantum numbers, $\pm \frac{1}{2}$ corresponding to quantized angular momenta, $\pm \frac{1}{2}h/2\pi$. The electron spin is associated with the interaction between an electron and an atom molecule or a system of atoms or molecules. Dirac

has shown the mathematical connection between the electron spin and the modification necessary to make Schroedinger's equation invariant under a Lorentz transformation.

The spin magnetic moment $\frac{e}{mc}\frac{h}{2\pi}$ associated with the spin angular momentum $\frac{1}{2}\frac{h}{2\pi}$ is important in the theory of magnetic properties of bodies. It reacts with the magnetic moments of the electron orbits. The moments are coupled when interaction is strong enough to produce a resultant from the orbital and spin moments. The coupled moment is space-quantized by a moderately strong external field and the electron transitions between the resulting levels then give the ordinary Zeeman effect of the corresponding main lines. A strong external field may break down the coupling so that the orbital and spin moments are space-quantized separately by the field. The transitions then give the Paschen-Bach effect. Coupling between spin and orbits increases rapidly with increasing atomic number.

The Pauli Exclusion Principle

Pauli's exclusion principal states that in a normal or excited atom no two electrons can have the same four quantum numbers, n, l, m, and s. The principle is closely connected with the general properties of wave functions. Assuming a discrete spectrum and neglecting interaction of particles, one would have k!-fold degeneracy for a system containing k identical particles. Letting the wave function of the fth particle, as a function of three co-ordinates and spin, be

expressed as $\psi_{\alpha_f}(r_{\beta_f})$, the k! linearly independent wave functions may be expressed $\psi_{\alpha_1}(r_{\beta_1})\psi_{\alpha_2}(r_{\beta_2})\psi_{\alpha_3}(r_{\beta_3})\ldots\psi_{\alpha_k}(r_{\beta_k})$ (39)

Other systems of k! linearly independent linear combinations may be used and the system must be considered when the interaction of the particles is treated as a perturbation.

$$\psi_s(1,2\ldots k) = \sum_{\substack{\text{all per-}\\ \text{mutations}}} \psi_{\alpha_1}(r_{\beta_1})\psi_{\alpha_2}(r_{\beta_2})\psi_{\alpha_3}(r_{\beta_3}) \ldots \psi_{\alpha_k}(r_{\beta_k}) \qquad (40)$$

and the determinant

$$\psi_\alpha(1,2,\ldots k) = \psi_\alpha(1,2,\ldots k) = \left|\psi_{\alpha_i}(r_{\beta_\ell})\right| \quad (i,e=1,2,\ldots k) \qquad (41)$$

which have simple structures are among the k! linear aggregates obtained. (40) is unaltered by interchange of any two particles and is symmetric; (41) changes sign and is antisymmetric when any two particles are interchanged. Taking the symmetric and anti-symmetric functions of the hydrogen molecule as $\psi_s(1,2)$ and $\psi_a(1,2)$, the proba- (42)
bility of transition from one state to the other is
$\int f(1,2)\,\psi_s(1,2)\,\psi_a(1,2)dv_1dv_2$ where f(1,2) is a function (43)
which is unaltered when the indistinguishable electrons are interchanged. Interchanging electrons changes only the variables of integration and the sign of $\psi_a(1,2)$. Consequently the integral vanishes and the conclusion must be that there are no transitions between symmetric and antisymmetric states.

More generally, the terms of a system containing n equal particles may be so divided into partial systems that only the terms belonging to a given partial system can combine

with each other. There will always be two partial systems in one of which the wave functions are symmetric, while in the other they are antisymmetric.

If the interaction of the particles is a symmetric function of their co-ordinates, the foregoing result holds for any interaction between the particles. The existence of two systems of terms between members of which there are no possible transitions implies that only one set of terms is applicable to a given type of structure such as an electron or photon. When the symmetric system is applicable to a structure, a definite distribution of the particles among the individual states corresponds to only a single wave function. When the anti-symmetric system is applicable, the wave function which corresponds to two particles in the same state always vanishes because the wave function changes sign when any two particles are interchanged. Therefore no two particles can be in the same state or have the same quantum numbers. Thus we see that the particles to which Pauli's exclusion principle applies require an antisymmetric term system.

The principle is not only applicable to electrons in atoms, but it may be applied to electrons in the hydrogen molecule with only a corresponding change in one quantum number; m is replaced by λ. The quantum numbers applicable to electrons in heavier molecules vary from K and L shells to the outer shells, but it may be stated that no two

electrons whose wave functions overlap may have identical quantum numbers.

The Quantum Number Λ

For molecules containing more than one electron, the quantum number for the cyclic co-ordinate φ is denoted by Λ. Where λ's may be assigned to individual electrons, it is equal to their algebraic sum. Values of Λ o,1,2,3, etc. are indicated by Σ, Π, Δ, Φ etc. From the energy values of the levels in the terms that have been interpreted with certainty and from the structure of the spectrum, it is apparent that only one electron is excited in the hydrogen molecule, while the other remains in the 1s state. Therefore λ for the excited electron would equal the Λ for the hydrogen molecule. Many lines have not been classified and other empirically established levels do not fit this theoretical scheme, however. Λ depends upon various interactions between the orbital and spin moments and the rotation and the relation of these to the internuclear axis. In the case of the hydrogen molecule, the electron spin interaction with the other motions is negligibly weak. Then Λ in the hydrogen molecule is made up of the contribution of the unexcited electron and the projection λ of the l of the excited electron on the internuclear axis. When hydrogen molecule has a low rotational quantum number, Λ interacts with the rotational impulse m which is constant in time and designated by the quantum number k.

Using arrows to indicate the angular momenta

$$\vec{K}^2 = \vec{m}^2 + \vec{\Lambda}^2 \qquad \text{or using quantum numbers} \tag{44}$$

$$\vec{m}^2 = \frac{h^2}{4\pi^2}\left[K(K+1) - \Lambda^2\right], \qquad K = 0,1,2\ldots. \tag{45}$$

The energy of the rotation terms is

$$E_{rot} = \frac{h^2}{8\pi^2 I}\left[K(K+1) - \Lambda^2\right] = hcB\left[K(K+1) - \Lambda^2\right] = hcW(K,\Lambda) \tag{46}$$

when $W(K,\Lambda)$ denotes the wave number equivalent of the energy. Absolute values of W can not be determined from the analysis of the structure of rotational partial bands, but the set of quantities $W(K+1) - W(K)$ can be determined for all admissible values of K. K must be equal to or greater than Λ. From (46) the possible values of Λ may be determined for many rotational bands. For those bands whose structure is too complicated for this method, other methods are available.

If F^r represents the rotational part of the energy, F^v the vibrational and F^{el} the electronic energy each divided by hc, the energies E of a molecule can be expressed:

$$E/hc = F^{el} + F^v + F^r \tag{47}$$

This is not exact due to the interplay of energies, but is a close approximation. F^r may be obtained from (46), F^v from (14) and F^{el} from (35). Successive values substituted in (47) give values of E/hc which may be substituted in (3). Values of ν thus obtained may be compared with values which were determined experimentally and recorded in Table II of this paper.

EXPERIMENTAL PROCEDURE

The Grating Spectrograph

The object of the research involved in this paper was to determine the wave lengths of molecular hydrogen in the region between $\lambda 5200$ Å and $\lambda 5800$ Å as recorded on a spectrogram containing comparison iron lines. Under the direction of the late Professor Norton A. Kent of Boston University, Dr. Reginald G. Lacount obtained this spectrogram by exposing an Eastman Spectroscopic Plate, Type I-D, in the thirty-foot Littrow mount spectrograph at Boston University.

On the following page is a diagram of the apparatus used by Dr. Lacount. G is a plane grating with 15,000 lines to the inch ruled by R. W. Wood. The light from the hydrogen discharge tube and the Pfund arc alternatively were focused by a lens and a large concave mirror, M_c, with focal length 97.3 cm on the slit, S. L_1, a six inch lens, rendered parallel the light entering the slit and after diffraction at G focused it on the photographic plate thirty feet from the lens at H. The Littrow mounting, based on the Rowland circle, has the grating and the photographic plate and slit at opposite ends of a chord on the Rowland circle.

The spectrograph was housed in a vibrationless insulating enclosure.

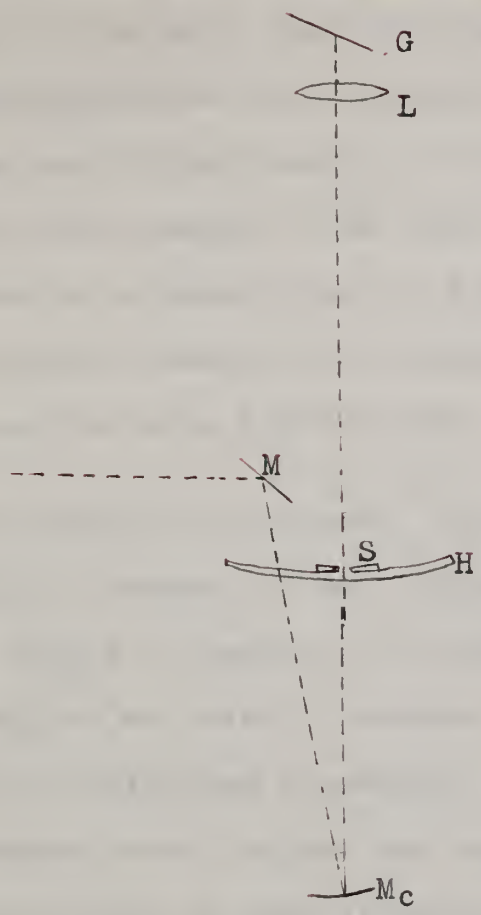


Figure 1

(Not drawn to scale)

G = Diffraction Grating
M = Plane Mirror. Front Silvered
M_c = Concave Mirror. Front Silvered
H = Plate Holder
S = Adjustable Slit
L = Achromatic Lens

The light from the hydrogen discharge tube was obtained when a 190 ma current at 14,000 volts was applied between the terminals of the tube, thus raising the molecules to an excited state from whence they returned to the ground state with the emission of light energy. The Pfund arc was used to produce the iron spectra. The lower and negative electrode consisted of a massive rod of iron with a depression in the top to hold a bead of iron oxide. The positive electrode consisted of a rod of iron.

Harrison Automatic Comparator and Microphotometer

The automatic comparator and microphotometer developed by Professor George R. Harrison in connection with the MIT Wavelength Project was used to measure the plate. This instrument was constructed to measure, compute, and record up to two thousand wave lengths per minute as well as a microphotometer trace of line intensities. A numbered dial is coupled by a continuously-moving shaft to the rest of the automatic recorder so that it moves with the plate. The wave length recordings are made when the dial is illuminated by a mercury arc flashed by a thyraton when there is a voltage drop of zero between two photocells. When the line is observed by only one cell the voltage drop is large. The cells are connected in opposition and their difference current is amplified, rectified, and impressed across a resistance to give this potential

difference. The spectral line interrupts first the beam of light going to one cell and later the beam going to the other.

The light falling on a third photocell causes an alternating current which is amplified, rectified, and fed through a moving-magnet oscillograph. The oscillograph traces the density curve on the moving film. To get to the photocells the light (1) passes through a disc which interrups it at the rate of three thousand times per second; (2) passes through the spectral plate; (3) falls on a slit and (4) is divided into three parts by glass rhombs. The wave lengths are recorded on 35 mm motion picture film for plate measurement (1) in the direction of decreasing wave length and (2) in the direction of increasing wave length. Approximately 16 Å are recorded on every foot of film. From the two films the average wave length was determined for each line.

Standard Lines

The primary standard of wave length adopted by the International Astronomical Union in 1938 was the red cadmium line $\lambda = 6438.4696$ Angstroms in dry air at 15° C on the hydrogen thermometer at a pressure of 760 mm of mercury with the value of g at 980.67 (45°). Certain secondary standards have also been adopted, most of which are lines in the spectrum of iron. Their source is the Pfund arc with an iron rod 6-7 millimeters in diameter as the upper electrode and a bead of iron oxide as the lower pole. The arc is

operated between 110 and 250 volts with 5 amperes or less at a length of 12-15 millimeters used over a central zone at right angles to the axis of the arc. Only lines measured concordantly and independently in at least three laboratories are accepted as standards. Certain of the most intense lines on the films corresponded to secondary iron standard lines in the region λ4918.999 to λ5615.652. Other intense lines beyond that region corresponding to tertiary hydrogen standard wave lengths were determined by the interferometric method and published by Dr. Lewis S. Combes. The difference between the standard and the averaged film lines were plotted against increasing wave length and a smooth parabolic curve drawn.

Since iron wave lengths were also recorded on the films, they had to be eliminated. The averaged corrected wave lengths were compared with iron lines from MIT and Transactions of the American Philosophical Society Tables and hydrogen lines from Table II of Mrs. E. B. Clancy's Master's thesis. The hydrogen lines determined by the foregoing procedure are recorded in Table II of this paper.

TABLES IA AND IB AND EXPLANATION

Table IA contains a list of secondary iron standard lines in Angstrom units in column (1), the corresponding wave lengths averaged from the two films in column (2), and the corrections which must be added to (2) in column (3). Table IB contains tertiary hydrogen standard lines in Angstrom units in column (1), the corresponding averaged film wave lengths in column (2), and the corrections which must be added to (2) in column (3).

TABLE IA

(1)	(2)	(3)
4918.999 Å	4919.082 Å	-0.083 Å
5012.071	5011.817	+0.254
5167.491	5167.020	+0.471
5328.534	5328.068	+0.466
5371.493	5371.110	+0.383
5405.778	5405.432	+0.346
5429.699	5429.399	+0.300
5455.613	5455.338	+0.275
5572.849	5572.891	-0.042
5586.763	5586.848	-0.085
5615.652	5615.849	-0.197

TABLE IB

(1)	(2)	(3)
5655.747	5656.010	-0.263
5728.456	5729.222	-0.676
5775.043	5775.946	-0.903
5806.095	5807.155	-1.060
5822.759	5823.899	-1.140

CORRECTION CURVE

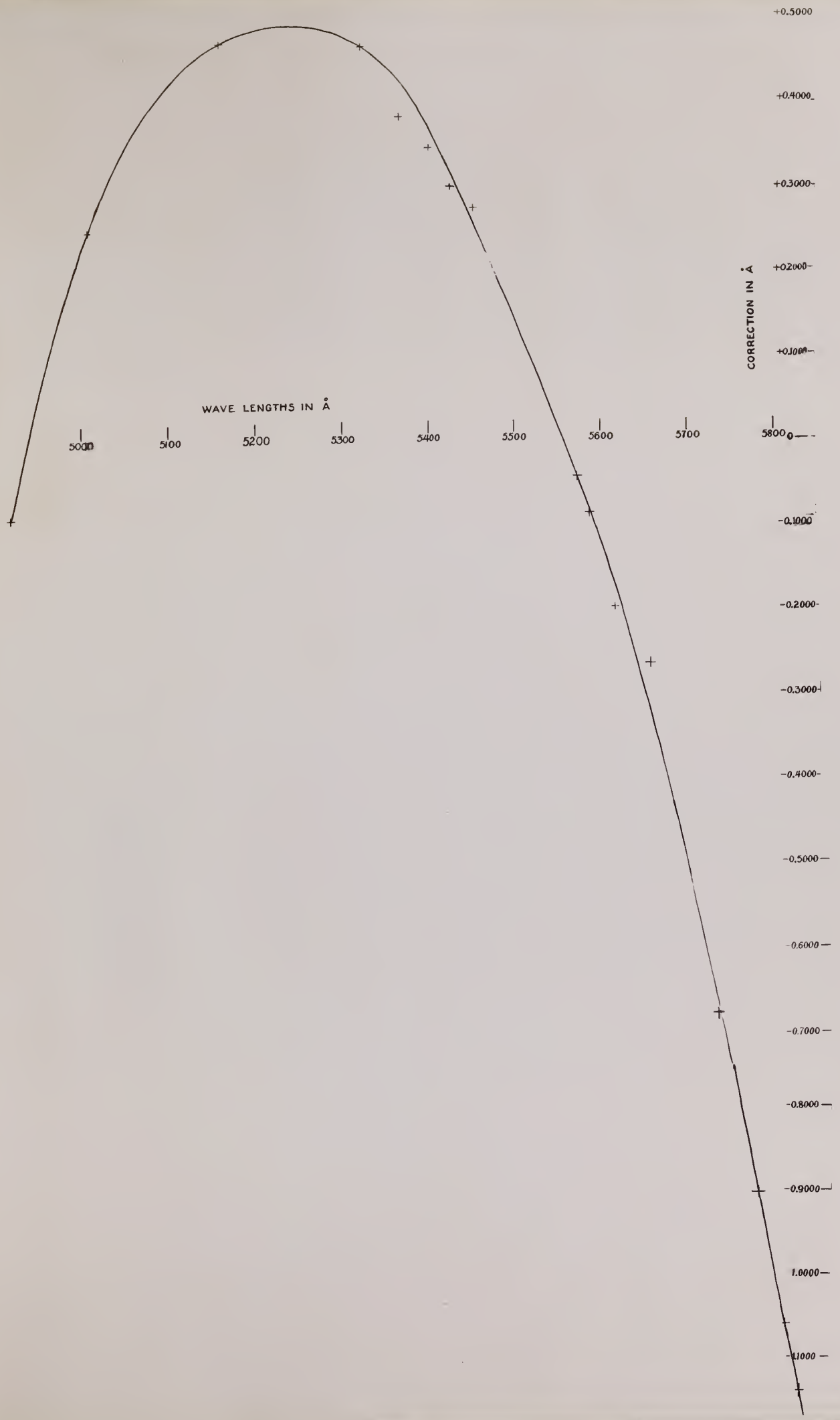
A small-scale photographic reproduction of the correction curve appears on the following page. The abscissa is expressed in terms of averaged lines from column (2) and the ordinates in terms of the corrections from column (3) Tables IA and IB.

The linear dispersion of a plane grating may be expressed as

$$\frac{dl}{d\lambda} = f \frac{n}{d \cos\beta}$$

where f is the distance of the image from the lens on its axis or the focal length of the lens forming the system, n is the order of diffraction, d is the grating constant, l is the distance along the plate and β is the angle of diffraction measured with respect to the normal to the grating. The dispersion is therefore a minimum when $\beta = 0$, and the spectrum is photographed normal to the grating. Since β is not zero throughout the region λ 5146 to λ5800, the correction curve is a cosine function.

For small values of the diffraction angle β the corrections are due almost entirely to departures from linearity in the dispersion and the curve is symmetric and regular.


WAVE LENGTHS IN Å
5000
5100
5200
5300
5400
5500
5600
5700
5800
CORRECTION IN Å
+0.5000
+0.4000
+0.3000
+0.2000
+0.1000
0
-0.1000
-0.2000
-0.3000
-0.4000
-0.5000
-0.6000
-0.7000
-0.8000
-0.9000
1.0000
-1.1000

I wish to express my appreciation to Prof. Taylor for his careful supervision of my thesis, to Dr. MacDonald for his helpful criticism, and to Dr. Frye for the presentation of the problem and numerous suggestions during the course of the work.

EXPLANATION OF TABLE II

Table II contains the pertinent data.

Column (4) is the intensity of each line, on an arbitrary scale of 0-8, measured approximately from the density tracings on the film.

Columns (5) and (6) are the wave lengths to ten-thousandths of an Angstrom unit, which were recorded by the automatic recorder on the two films.

Column (7) is the average of these readings to ten-thousandths of an Angstrom unit.

Column (8) is an average of these readings to a thousandth of an Angstrom unit.

Column (9) is the correction interpolated from the correction curve. It is read in thousandths of an Angstrom unit.

Column (10) is the corrected wave length to seven figures.

Column (11) is the wave number, in air, which is the reciprocal of the wave length given in (10).

Wave numbers are more useful in carrying out theoretical calculations since they represent the difference between two energy states or levels. Wave numbers in column (11) could be compared with values calculated by substituting in (3) energies determined in (47).

Many of the lines occuring on the spectrogram and consequently listed on the films could not be identified as either iron or molecular hydrogen lines. The spectrogram

was marked molecular deuterium as well as iron and molecular hydrogen. Comparison with a plate containing deuterium alone proved, that if present at all, the amount of deuterium was very negligible. The unidentified lines may be due to deuterium or DH or may be unidentified iron or molecular hydrogen lines.

In many cases where strong iron lines occur, less intense hydrogen lines in the vicinity were not recorded on either film. This difficulty occurs because the A and C slope does not come to zero for the less intense line (See Procedure). No attempt has been made to include such lines since they are quite numerous and their accuracy would necessarily be low.

TABLE II

(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
7	51458670	51458881	51458776	5145878	459	5146337	19431296
0	69020	69209	69115	6912	460	7372	27389
2	72867	73065	72966	7297	460	7757	25936
1	79660						
2	95717	95966	95842	9584	462	5150046	17302
2	51529416	51529631	29524	2952	464	3416	04605
6	33861	34073	33967	3397	464	3861	02929
1	40100	40062	40081	4008	464	4472	00625
1		46958					
2	57711	57947	57829	5783	465	6248	19393947
4	63547	63769	63658	6366	466	6832	91751
1	74067	74291	74179	7418	466	7884	87795
2	76836	77052	76944	7694	467	8161	86754
2	79001	79212	79107	7911	467	8378	85939
2	83587	83826	83707	8371	467	8838	84210
3	93502	93721	93612	9361	467	9828	80491
2	51600593	51600814	51600704	5160070	468	5160538	77825
1	27037	27258	27148	2715	470	3185	67890
1		33992					
2		39545					
3	42261	42483	42372	4237	470	4707	62183
6	77500	77717	77609	7761	472	8233	48973
2	91134	91392	91263	9126	473	9599	43860
1	98722	98963	98843	9884	473	5170357	41024
3	51704278	51704487	51704383	5170438	474	0912	38948
1	20366	20545	20456	2046	474	2520	32936
1	23839	24049	23944	2394	474	2868	31636
3	32866	33062	32964	3296	475	3771	28262
1	34782	35017	34900	3490	475	3965	27537
7	42065	42278	42172	4217	475	4692	24822
1	47691	47921	47806	4781	476	5257	22712
1	62761	62960	62861	6286	476	6762	17094
2	79897	80066	79982	7998	477	8475	10704
0	91573						
7	51800881	51801078	51800980	5180098	478	5180576	02873
1	08285	08461	08373	0837	478	1315	00120
1	15254						
1	22431	22657	22544	2254	479	2733	19294839
1	30841	31050	30946	3095	479	3574	91709
1	46082	46241	46162	4616	480	5096	86046
1	49172	49452	49312	4931	480	5411	84874
1	51650	51823	51737	5174	480	5654	83971
1	59897						
4	77822	78010	77916	7792	481	8273	80019
1	89672	89870	89771	8977	482	9459	69831

1	51895001	51895169	51895085	5189509	482	5189991	19267856
2	98932	99107	99020	9902	482	5190384	66397
5	51905360	51905542	51905451	5190545	482	1027	64011
3	25068	25250	25159	2516	483	2999	56695
1	31209	31384	31297	3130	483	3613	54419
8	58726	58927	58827	5883	484	6367	44214
2	62039						
7	67242	67434	67338	6734	484	7218	41063
5	71040	71220	71130	7113	484	7597	39660
1	75209						
1	84750						
4	88229	88412	88321	8832	485	9317	33295
6	92145	92331	92238	9224	485	9709	31845
2		52015639					
3	52025191	25388	52025290	5202529	486	5203015	19626
1		35426					
3	38462	38622	38542	3854	486	4340	14732
3	45657	45864	45761	4576	486	5062	12067
2	50329	50537	50433	5043	486	5529	10343
0	85250	85427	85339	8534	487	9021	19197465
2	52110014	52110203	52110109	5211011	488	5211499	88337
2	26489	26782	26636	2664	488	3152	82253
6	41131	41307	41219	4122	488	4610	76890
4	50960	51130	51045	5105	489	5594	73272
1	80642						
1	87706						
1	98811						
3	52206447	52206588	52206518	5220652	490	5221142	52898
3	09444	09601	09523	0952	490	1442	51798
4	20939	21060	21000	2100	490	2590	47588
6	23522	23657	23590	2359	490	2849	46638
4	30405	30548	30477	3048	490	3538	44113
4	39007	39127	39067	3907	490	4397	40965
2	43376	43511	43444	4344	490	4834	39364
8		63958					
3	87311	87537	87424	8726	490	9216	23333
4	91086	91188	91137	9114	490	9604	21907
2	99627	99762	99695	9970	491	5230461	18774
0		52304431					
3	52312651	12763	52312707	5231271	491	1762	14019
2	29175						
1	45913	46014	45964	4596	491	5087	01879
1	56236	56343	56290	5629	491	6120	98111
5	85218	85331	85275	8528	491	9019	87543
1	94180	94308	94244	9424	491	9915	84279
1	52402830	52402890	52402890	5240289	491	5240780	81129
1		05710					
1	08070	08181	08126	0813	491	1304	79222
4	32349	32472	32411	3241	491	3732	19070387
2	41439	41576	41508	4151	491	4642	67078
2	51218	51334	51276	5128	491	5619	63527

1	52454252	52454307	52454280	5245428	491	5245919	19062437
2	68800	68909	68855	6886	491	7377	57140
1	70906	71019	70963	7096	491	7587	56378
0	73162						
1	74488	74606	74547	7455	491	7946	55074
1	92229	92334	92282	9228	491	9719	48639
3	97092	97192	97142	9714	491	5250205	46875
2	52520814	52520926	52520870	5252087	491	2578	38270
1	32218						
8	61177	61285	61231	6123	491	6614	23653
2	66009	66120	66065	6607	491	7098	21901
2	71418	71534	71476	7148	491	7639	19944
2	80356	80474	80415	8042	491	8533	16711
2	88932	89042	88987	8899	490	9389	13615
2	94151	94258	94205	9421	490	9911	11729
7	52606907	52607011	52606959	5260696	490	5261186	07121
1	17596	17670	17633	1763	490	2253	03267
4	31221	31320	31271	3127	490	3617	18998343
6	33958	34063	34011	3401	490	3891	97354
4	37980	38083	38032	3803	490	4293	95903
6	41940	42042	41991	4199	490	4689	94474
1	49780	49869	49825	4983	490	5473	91646
8	55522	55681	55602	5560	490	6050	89565
2	65550						
2	77519	77619	77569	7757	489	8246	81650
8	52718067	52718215	52718141	5271814	489	5272303	67043
6	28863	28965	28914	2891	489	3380	63170
3	33362	33471	33417	3342	488	3830	61552
2	36030	36147	36089	3609	488	4097	60592
2	58062	58190	58126	5813	488	6301	52672
1	65832	65929	65881	6588	488	7076	49888
2	68996	69103	69050	6905	488	7393	48750
3	73096	73189	73143	7314	488	7802	47281
5	78493	78601	78547	7855	488	8343	45339
2	91450	91579	91515	9152	487	9639	40689
2	98699	98836	98768	9877	487	5280364	38088
2	52800949	52801081	52801015	5280102	487	0589	37281
1	05935	05993	05964	0596	487	1083	35510
1	24439	24550	24495	2450	486	2936	28868
6	28014	28109	28062	2806	486	3292	27593
7	40091	40220	40156	4016	486	4502	23259
2	86263	86382	86325	8632	485	9117	06748
2	89908	90022	89965	8997	484	9481	05446
2	98961	99071	99016	9902	484	5290386	02212
7	52911094	52911232	52911163	5291116	484	1600	97876
1	45575						
1	63722	63812	33767	6377	482	6859	79113
2	71372	71527	71450	7145	482	7627	76376
1	84878	85011	84945	8495	481	8976	71571
2	88053	88151	88102	8810	481	9291	70449
4	92291	92414	92353	9235	481	9716	68936

1	52997121	52997236	52997179	5299718	481	5300199	18867216
6	53016491	53016627	53016559	5301656	480	2136	60323
2	21405	21542	21474	2147	480	2627	58577
8	26391	26613	26502	2650	480	3130	56788
2	34659	34735	34697	3470	480	3950	53873
7	39384	39520	39452	3945	479	4424	52188
2	50973	51084	51029	5103	479	5582	48074
4	81869	81982	81926	8193	478	8671	37106
7	85644	85785	85715	8572	478	9050	35762
2		97685					
1	53110903	53111020	53110962	5311096	476	5311572	26818
2	26774	26872	26823	2682	475	3157	21202
4	31350	31482	31416	3142	475	3617	19572
2	38863	39013	38938	3894	475	4369	16909
2	46765	46940	46853	4685	474	5159	14113
3	48848						
1	53140	53318	53229	5323	474	5797	11855
2	57083						
7	74262	74428	74345	7435	473	7908	04387
1	78858						
6	86994	87134	87064	8706	472	9178	18799897
1	92626						
4	99706	99842	99774	9977	471	5320448	95410
4	53210351	53210492	53210422	5321042	471	1513	91648
1	18737	18858	18798	1880	470	2350	88693
1	44982	45167	45075	4508	469	4977	79424
1	50786	50912	50849	5085	468	5553	77392
2	85671	85837	85754	8575	466	9041	65102
3	91899	92064	91982	9198	465	9663	62912
2	95158	95309	95234	9523	465	9988	62768
1	53302276						
2	08109	53308299	53308204	5330820	464	5331284	57207
3	11575	11745	11660	1166	464	1630	55990
1	17022	17168	17095	1710	464	2174	54077
7	38155	38323	38239	3824	462	4286	46651
2	48244	48424	48334	4835	461	5294	43110
5	58939	59090	59015	5902	461	6363	39355
7	61346	61533	61440	6144	460	6604	38509
1	72343	72501	72422	7242	460	7702	34654
2	75701	75926	75814	7581	459	8040	33468
0	82146						
2	86910	87058	86984	8698	458	9156	29552
8	53405653	53406046	53405850	5340585	458	5341043	22935
1	12157	12400	12279	1228	457	1685	20685
4	27199	27392	27296	2730	455	3185	15429
3	38040	38226	38133	3813	454	4267	11640
6	43231	43430	43331	4333	454	4787	09819
2	53925	54134	54030	5403	453	5856	06078
1	97930	98148	98039	9804	449	5350253	18690705
2	53502769	53502956	53502863	5350286	449	0735	89021
4	13038	13221	13130	1313	448	1761	85438
1	18259	18492	18366	1837	447	2284	83612

1	53537512						
6	43302	53543509	53543406	5354341	445	5354786	18674883
7	54793	55000	54897	5490	444	5934	70878
5	68416	68614	68515	6852	442	7294	66140
2	77999	78183	78091	7809	441	8350	62461
4	82829	83046	82938	8294	441	8735	61121
2	88252	88486	88369	8837	440	9277	59233
1	89970						
2	95034	95262	95148	9515	439	9954	56877
0	53603191						
2	11610	53611831	53611721	5361172	437	5361609	51118
2	30967	31164	31066	3107	436	3543	44392
7	54759	54990	54875	5488	434	5922	36126
3	79285	79512	79399	7940	432	8372	27621
2	84088	84303	84196	8420	431	8851	25959
3	89901	90099	90000	9000	430	9430	23951
2	53700741						
7	14608						
6	20323	53720560	53720442	5372044	425	5372469	13416
5	26841	27061	26951	2695	424	3119	11164
6	30000	30222	30111	3011	423	3434	10073
2	39139	39357	39248	3925	422	4347	06912
1	41652	41882	41767	4177	422	4599	06039
1	44869	45083	44976	4498	422	4920	04928
1	51923	52157	52040	5204	421	5625	02488
2	60397	60602	60500	6050	419	6469	18599568
2	68234	68441	68338	6834	418	7252	96860
6	79897	80102	80000	8000	416	8416	92835
4	91373	91570	91472	9147	414	9561	88877
2	95598	95773	95686	9569	414	9983	87419
1		53805041					
6	53851085	51280	53851183	5385118	405	5385523	68299
5	58037	58228	58133	5813	404	6217	56906
2	60743	61001	60872	6087	404	6491	64962
5	63480	63670	63575	6358	403	6761	64031
4	71315	71500	71408	7141	402	7543	61337
8	77652	77900	77776	7778	401	8179	59146
2	53901368	53901547	53901458	5390146	397	5390543	51007
4	07942	08129	08036	0804	396	1200	48746
4	11356	11556	11456	1146	395	1541	47573
7	19121	20311	19716	1972	394	2366	44735
1	32713	32864	32789	3279	393	3672	40245
2	37349	37516	37433	3743	390	4133	38660
3	39929	40103	40016	4002	390	4392	37770
4	44168	44350	44259	4426	389	4815	36317
3	77159	80304	78732	7873	384	8257	24498
6	85965	86142	86054	8605	382	8987	21993
4	94537	94707	94622	9462	380	9842	19060
7	54006752	54006922	54006837	5400684	378	5401062	14877
3	13895	14058	13977	1398	377	1775	12433
2	17133	17299	17216	1722	376	2098	11327
1	22120	22276	22198	2220	375	2595	09624

5	54043944	54044115	54044030	5404403	370	5404773	18502165
6	49854	50032	49943	4994	369	5363	00145
2	64099	64281	64190	6419	366	6785	18495280
2		66979					
5	84339	84521	84430	8443	362	8805	88372
6	93481	93652	93567	9357	361	9718	85252
2	98714	98867	98791	9879	358	5410237	83479
1	54111078	54111198	54111138	5411114	356	1470	79267
1	55741	55910	55826	5583	347	5930	46050
8	74562	74776	74669	7467	342	7809	57646
1	80305						
2	83184	83372	83278	8328	340	8668	54720
8	95460	95785	95623	9562	337	9899	50528
4	54203804	54203962	54203883	5420388	335	5420723	47724
4	09926	10092	10009	1001	334	1335	45641
5	17824	17979	17902	1790	333	2123	42960
4	29592	29785	29639	2964	330	3294	38978
7	48622	48783	48703	4870	326	5196	32514
8	55725	55912	55819	5582	325	5907	30098
5	59405	59548	59477	5948	323	6271	28862
5	61475	61632	61554	6155	322	6477	28163
2	78030	78184	78107	7811	319	8130	22551
2	80598	80756	80677	8068	318	8386	21682
5	86426	86590	86508	8651	317	8968	19707
5		90394					
4	98548	98703	98626	9863	315	5430173	15603
5	54305709	54305844	54305777	5430578	313	0891	13185
2	20035	20173	20107	2011	310	2321	08338
1	28169	28295	38232	2823	308	3131	05593
2	33128	33283	33206	3321	307	3628	03910
8	45000	45171	45086	4509	304	4813	18399897
1		58246					
4	84803	84961	84882	8488	295	8783	86466
3	93730	93908	93819	9382	294	9676	83448
5	98788	98941	98865	9887	292	5440179	81748
1	54404328	54404484	54404406	5440441	290	0731	79883
1	22159	22302	22231	2223	286	2509	73879
1	30839	30998	30919	3092	284	3376	70952
1	40609	40739	40674	4067	280	4347	67676
3	71281	71470	71376	7138	275	7413	57338
1	95881	96073	95977	9598	269	9867	49072
1	54510232	54510430	54510331	5451033	266	5451299	44252
3	18340	18526	18433	1843	264	2107	41533
3	22650	22812	22731	2273	263	2536	40090
1	39018	39241	39130	3913	260	4173	34585
2	44680	44846	44763	4476	258	4734	32700
3	64569	64738	64654	6465	254	6719	26031
6	67276	67454	67365	6737	253	6990	25121
2	76642	76825	76734	7673	252	7925	21981
2	85521	85724	85623	8562	248	8810	19011
7	93415	93598	93507	9351	247	9598	16367
5	54611589	54611768	54611679	5461168	242	5461410	10290

3	54615605	54615779	54615692	5461569	240	5461809	18308952
2	20483	20676	20580	2058	239	2297	07317
7	27535	27748	27642	2764	238	3002	04954
5	61989	62179	62084	6208	229	6437	18293451
3	82953	83129	83041	8304	224	8528	86457
2	98883	99057	98970	9870	220	5470117	81145
2	54703202	54703393	54703298	5470330	220	0550	79698
3	13551	13732	13642	1364	218	1582	76250
2	30953	31118	31036	3104	213	3317	70456
1	39766						
7	46301	46491	46396	4640	210	4850	65341
6	63451	63631	63541	6354	205	6559	59641
2	69560	69522	69441	6944	203	7147	57681
2	76180	76350	66265	7627	202	7829	55407
2	86794	86968	86881	8688	200	8888	51879
0		54801874					
8	54808664	08878	54808771	5480877	194	5481071	44609
0	21722	21900	21811	2181	191	2372	40280
2	26378	26553	26466	2647	190	2837	38733
2	37790	37989	37890	3789	187	3976	34945
3	55205	55379	55292	5529	183	5712	29174
2	70855	71058	70957	5096	179	7275	23982
2	99591	99752	99672	9967	172	5490139	14475
2	54910781	54910971	54910876	5491088	170	1258	10763
4	27972	28148	28060	2806	165	2971	05084
1	46350	46539	46445	4645	161	4806	18199005
1	50096	50289	50193	5019	160	5179	97769
7	57880	58058	57969	5797	158	5955	95200
3	63936	64100	64018	6402	156	6558	93204
4	70332	70505	70419	7042	154	7196	91092
2	83789	83951	83870	8387	151	8538	86653
4	90348	90527	90438	9044	150	9194	84483
8	94103	94300	94202	9420	149	9569	83243
4	50003370	50003553	50003466	5000347	146	5500493	80189
1	34867						
8	53586	53791	53689	5369	134	5503	63645
7	61843	62020	61932	6193	132	6325	60933
6	76893	77073	76983	7698	129	7827	55981
1	90704	90865	90785	9079	125	9204	51443
1	92409	92562	92486	9249	124	9373	50886
2	55101231	55101389	55101310	5510131	122	5510253	47987
2	28254	28417	28336	2834	115	2949	39112
2	37834	38000	37917	3792	113	3905	35967
2	44381	44549	44465	4447	111	4558	33820
0		76752					
2	78924	79098	79011	7901	102	8003	22498
7	83438	83627	83533	8353	101	8454	21017
5	55207669	52207832	55207751	5520775	95	5520870	13087
2	17255	17439	17347	1735	93	1828	09945
1	26148	26382	26265	2627	90	2717	07030
4	38443	38618	38531	3853	87	3940	03021
3	40396	40572	40484	4048	87	4135	02382

1	55257124	55257320	55257222	5525722	83	5525805	18096911
4	62131	62311	62221	6222	81	6303	95280
5	72476	72662	72569	7257	79	7336	91898
2	76910	77076	76993	7699	78	7777	90455
2	80983	81164	81074	8107	76	8183	89126
1	90866	91049	90958	9096	74	9170	85897
2	94322	94499	94411	9441	73	9514	84772
2	97740	97935	97838	9784	72	9856	83654
1	55310376						
4	39846	40025	55339936	5533994	62	5534056	69929
1	44019	44190	44105	4411	61	4472	68571
0		51211					
7	59071	59251	59161	5916	56	5972	63675
2	63030	63189	63110	6311	55	6366	62390
8	73783	74124	73954	7395	53	7448	58830
2	85674	85911	85793	8579	51	8630	55006
2	98991	99132	99062	9906	46	9952	50698
1		55406305					
3	55408960	09125	55409043	5540904	43	5540947	47457
1	19823	19986	19905	1991	40	2031	43926
1	22277	22428	22353	2235	39	2274	43135
1	25189	25323	25256	2526	38	2564	42191
7	30758	30910	30834	3083	37	3120	40382
7	34489	34652	34571	3457	36	3493	39168
3	47104	47268	47186	4719	33	4752	35072
2	64573	64730	64652	6465	29	6494	29407
4	76181	76364	76273	7627	26	7653	25641
2	83728	83865	83797	8380	24	8404	23201
3	94587	94736	94662	9466	20	9486	19687
4	97195	97337	97266	9727	20	9747	18839
1	55500198	55500345	55500272	5550027	19	5550046	17869
2	03336	03470	03403	0340	18	0358	16856
2	09930	10071	10001	1000	17	1017	14717
8	24978	25150	25064	2506	13	2519	09844
3	39057	39201	39129	3913	9	3922	05294
6	50830	50969	50900	5090	6	5096	01489
1	57427	57515	57471	5747	4	5751	17999367
2	64775	64903	64839	6484	3	6487	96982
2	73782	73917	73850	7385	0	7385	94075
2	79451	79633	79542	7954	-1	7953	92236
3	89259	89400	89330	8933	-4	8929	89077
1	97249	97319	97284	9728	-6	9722	86511
3	55601651	55601772	56601712	5560171	-7	5560164	85081
2	14467	14592	14530	1453	-11	1442	80948
6	17427	17561	17494	1749	-11	1738	79991
3	22495	22628	22562	2256	-13	2243	78359
1		31359					
6	45206	45337	45272	4527	-19	4508	71041
2	48993	49106	49050	4905	-20	4885	69823
5	61569	61695	61632	6163	-24	6139	65775
1	77699	77828	77764	7776	-27	7749	60580
2	55716235	55716349	55716292	5571629	-38	5571591	48195

1		55735758					
6	55739625	39749	55739687	5573969	-45	5573924	17940682
4	87601	87722	87662	8766	-58	8708	25297
3	94172	94277	94225	9425	-60	9363	23193
4	96519	96642	96581	9658	-61	9597	22441
0		55806586					
1	55819931	20035	55819983	5581998	-67	5581931	14947
3	31054	31192	31123	3112	-71	3041	11386
1		44346					
2	55430	55551	55491	5549	-76	5473	03587
2	60291	60429	60360	6036	-78	5958	02032
2	76030	76152	76091	7609	-83	7526	17897008
3	55901913	55902072	55901993	5590199	-90	5590109	88739
2	10760	10901	10831	1083	-93	0990	85920
3	15180	15327	15254	1525	-94	1431	84509
1	35505						
2	38918	39054	38986	3899	-101	3798	76942
2	43213	43377	43295	4330	-103	4227	75571
2	50981						
1	72070						
8	77589	77795	77692	7769	-113	7656	64620
4	84223	84387	84305	8431	-116	8315	62518
2	90289	90441	90365	9037	-117	8920	60587
2	96210	96379	96295	9630	-118	9512	58699
7	56005360	56005529	56005445	5600545	-121	5600424	55791
4	17809	17968	17889	1789	-125	1664	51838
1	23752						
5	28702	28871	28787	2879	-129	2750	48378
2	41884	42032	41958	4196	-133	4063	44196
3	44761	44910	44836	4484	-134	4350	43282
5	48381	48536	48459	4846	-135	4711	42133
1	70432	70575	70504	7050	-142	6908	35142
1	83043	83177	83110	8311	-146	8165	31144
1	97032	97302	97167	9717	-151	9566	26691
1	56120780	56120901	56120841	5612084	-158	5611926	19194
8	27159	27369	27264	2726	-161	2565	17166
1	36520	36682	36601	3660	-163	3497	14207
5	63971	64123	64047	6405	-172	6233	05529
1	70219	70382	70301	7030	-174	6856	03554
1	77062						
2	84898	85040	84969	8487	-179	8318	17798921
2	56202060	56202209	56202135	5620214	-186	5620028	93506
7	11175	11331	11253	1125	-189	0936	90631
2	28361	28502	28432	2843	-195	2648	85214
5	32971	33114	33043	3304	-196	3108	83759
6	45244	45372	45308	4531	-200	4331	79892
1	58731	58884	58808	5881	-206	5675	75645
2	61323	61463	61393	6139	-206	5933	74830
2	69479	69629	69554	6955	-209	6746	72261
4	76556	76711	76634	7663	-211	7452	70032
1	56300412	56300551	56300482	5630048	-221	9827	62535
7	08597	08743	08672	0867	-223	5630644	59958

5	56312362	56312512	56312457	5631244	-225	5631019	17758775
2	20178	20330	20254	2025	-228	1797	56322
4	24529	24670	24600	2460	-230	2230	54957
6	44248	44402	44325	4433	-237	4196	48761
3	47071	47210	47141	4714	-238	4476	47879
8	50575	50771	50673	5067	-239	4828	46771
2	58345	58496	58421	5842	-242	5600	44340
1	78358						
2	92842	92977	92910	9291	-256	9035	33531
2	56407042	56407192	56407117	5640712	-262	5640450	29082
2	17405	17542	17474	1747	-266	1481	25842
2	23441	23565	23503	2350	-268	2082	23954
6	30072	30225	20149	3015	-270	2745	21817
6	32341	32494	32418	3242	-271	2971	21161
3	64074	64222	64148	6415	-285	6130	11246
1	77132	77256	77194	7719	-290	7429	07173
2	91531	91698	91615	9162	-295	8867	02665
1	56509927	56510062	56509995	5651000	-302	5650698	17696929
4	25048	25200	25124	2512	-308	2204	92214
2	28758	28921	28840	2884	-310	2574	91055
4	50722	50858	50790	5079	-318	4761	84213
8	60900	61093	60997	6100	-322	5778	81033
2	64575	64758	64667	6467	-325	6142	79896
3	76672	76815	76744	7674	-328	7346	76133
5	81469	81642	81556	8156	-331	7825	74636
3	97919	98052	97986	9799	-337	9462	69524
1		56603039					
3	56611615	11739	56611677	5661168	-343	5660825	65270
2	14539	14669	14604	1460	-345	1115	64365
7	19969	20110	20040	2004	-347	1657	62674
6	22034	22160	22097	2210	-348	1862	62034
6	32561	32698	32630	3263	-352	2911	58762
1	37922	38020	37971	3797	-354	3443	57104
1	60238						
3	77552	77673	77613	7761	-370	7391	44803
2	87638	87732	87685	8769	-375	8394	41681
2	97228	97342	97285	9729	-378	9351	38703
3	56706853	56706958	56706906	5670691	-382	5670309	35723
7	13329	13459	13394	1339	-385	0954	33717
2		27889					
5	30330	30453	30392	3039	-393	2646	28458
2	49277	49393	49335	4934	-401	4533	22596
7	53568	53721	53645	5365	-403	4962	20012
2	66011	66120	66066	6607	-405	6202	17414
1	70361	70478	70420	7042	-409	6633	16076
1	74880	74985	74932	7493	-411	7082	14683
2	78434	78564	78499	7850	-412	7438	13579
1		88783					
1	56805912	56806066	56805989	5680599	-425	5680174	05094
1		19422					
1	25602	25715	25659	2566	-434	2132	17599028
5	29692	29812	29752	2975	-435	2540	97764

6	56835432	56835555	56835494	5683549	-438	5683111	17595996
6	42150	42285	42222	4222	-441	3781	93922
8	45972	46139	46056	4606	-443	4163	92740
4	49883	50006	49945	4995	-444	4551	91539
1	62766	62794	62780	6278	-450	5828	87588
2	67309	67455	67382	6738	-453	6285	86174
1		74122					
3	79461	79580	79521	7952	-458	7494	82436
3	84092	84225	84159	8416	-461	7955	81011
8	96690	97116	96903	9690	-465	9225	77087
2		56903661					
6	56916577	16699	56916638	5691664	-474	5691190	71018
4	26074	26195	26135	2614	-480	2134	68104
3	29634	29737	29686	2969	-482	2487	67014
8	46507	46657	46582	4658	-490	4168	61828
5	66950	67062	67006	6701	-501	6200	55563
2	73948	74037	73993	7399	-504	6895	53422
6	79558	79670	79614	7961	-506	7455	51696
3	85291	85402	85347	8535	-510	8025	49941
1	89767						
4	95950	96069	96010	9601	-515	9086	46673
7	57011835	57011970	57011903	5701190	-525	5700665	41813
1	29553	29641	29597	2960	-533	2427	36393
8	37968	38110	38039	3804	-536	3268	33807
8	43016	43169	43093	4309	-540	3769	32267
1	51019	51117	51068	5107	-544	4563	29827
2	60564	60701	60633	6063	-548	5515	26902
2	92302	92413	92358	9236	-564	8672	17209
7	57103526	57103648	57103587	5710359	-571	9788	13785
3		26608					
6	37286	37397	37342	3734	-587	5713147	03488
8	40393	40519	40456	4046	-589	3457	02538
7	51782	51889	51836	5184	-595	4589	17499071
1		59839					
7	66125	66235	66180	6618	-602	6016	94703
1	88814	88892	88853	8885	-612	8273	87797
3	93137	93250	93194	9319	-616	8703	86483
3	57201380	57201476	57201428	5720143	-618	9525	83969
2	07789						
2	30430						
8	40853	40981	40917	4092	-638	5723454	71967
3	49115	49203	49159	4916	-643	4273	69467
3	52666	52762	52714	5271	-644	4627	68387
5	65377	65488	65433	6543	-650	5893	64525
2	73292	73410	73351	7335	-654	6681	62122
7	77111	77229	77170	7717	-656	7061	60963
8	92011	92129	92220	9222	-664	8558	56400
3	98902	98995	98949	9895	-666	9229	54356
3	57310316	57310419	57310368	5731037	-673	5730364	50898
2	13303	13410	13357	1336	-674	0662	49991
8	25991	26204	26098	2610	-680	1930	46131
3	39437	39523	39480	3948	-686	3262	42077

4	57342530	57342620	57342575	5734258	-688	5733570	17441141
3	51980	52087	52034	5203	-693	4510	38282
8	58337	58489	58413	5841	-696	5145	36351
8	75708	76278	75993	7599	-705	6894	31035
2	82145	82220	82183	8218	-708	7510	29164
1	87568	87666	87617	8762	-712	8050	27523
7	91302	91420	91361	9136	-713	8423	26390
7	57408109	57408222	57408166	5740817	-722	5740095	21314
2	12446	12559	12503	1250	-724	0526	20006
4	14919	15004	14962	1496	-725	0771	19263
2	18404	18495	18450	1845	-727	1118	18210
3	21200	21293	21247	2125	-729	1396	17367
6	25542	25642	25592	2559	-732	1827	16059
5	39336	39457	39397	3940	-738	3202	11890
5	46557	46661	46609	4661	-742	3919	09716
4	61229	61322	61276	6128	-750	5378	05295
3	70651	70756	70704	7070	-756	6314	02480
1	82692	82809	82751	8275	-760	7515	17398824
4	97616	97769	97693	9769	-769	9000	94329
3	57519198	57519317	57519258	5751926	-779	5751147	87836
3	23342	23436	23389	2339	-783	1556	86599
1	31162	31281	31222	3122	-786	2336	84242
2	36566	36666	36616	3662	-789	2873	82619
4	43500	43592	43546	4355	-794	3561	80541
2	54482	54593	54538	5454	-800	4654	77239
0	57402						
8	64838	64973	64906	6491	-805	5686	74124
4	73500	73618	73559	7356	-810	6546	71528
8	81808	82053	81931	8193	-813	7380	69012
2	87926	88028	87977	8798	-817	7981	67199
2		92126					
8	57603671	57603829	57603750	5760375	-825	9550	62468
8	11977	12158	12068	1207	-829	5760378	59972
2		20338					
7	35478	35602	35540	3554	-841	2713	52938
3	48888	48949	48919	4892	-848	4044	48931
6	67423	67529	67476	6748	-857	5891	43373
7	71343	71482	71413	7141	-859	6282	42197
7	78408	78523	78466	7847	-860	6987	40077
1	91216	91312	91264	9126	-869	8257	36259
4	57710490	57710575	57710533	5771053	-879	5770174	30500
2	13369	13461	13415	1342	-880	0462	29635
5	33327	33437	33382	3338	-890	2448	23673
3	36110	36200	36155	3616	-891	2725	22841
8	40733	40983	40858	4086	-893	3193	21437
1	47671						
8	54823	54951	54887	5489	-900	4589	17250
8	59262	59656	59459	5946	-902	5044	15885
2	90522	90643	90583	9058	-918	8140	06607
8	98952	99127	99040	9904	-922	8982	04086
2	57806349	57806401	57806375	5780638	-926	9712	01900

8	57809948	57810097	57810023	5781002	-929	5780073	17300820
5	16345	16459	16401	1640	-932	0708	17298919
4	32272	32377	32325	3233	-940	2293	94177
7	39404	39532	39468	3947	-943	3004	92051
2	50338	50441	50390	5039	-949	4090	88804
6	53554	53657	53606	5361	-951	4410	87848
8	61642	61787	61715	6172	-954	5218	85433
8	66993	67527	67260	6726	-958	5768	83790
5	76280	76389	76335	7634	-961	6673	81087
2	84898	84992	84945	8495	-967	7528	78534
4	87917	88012	87965	8797	-968	7829	77636
8	92293	92473	92383	9238	-969	8269	76322
7	57908513	57908632	57908573	5790857	-979	9878	71521
8	26830	27049	26940	2694	-987	5791707	66067
3	34793	34869	34831	3483	-992	2491	63730
1	38246	38356	38302	3830	-993	2837	62699
8	56187	56298	56243	5624	-1000	4624	57375
2	64499	64575	64537	6454	-1006	5448	54921
5	69945	70022	69984	6998	-1008	5990	53308
6	76207	76313	76260	7626	-1010	6616	51445
6	83808	83903	83856	8386	-1013	7373	49192
7	99753	99877	99815	9982	-1022	8960	44471

SOURCES OF ERROR

The accuracy of the wave lengths is affected by the following:

(1) Since the spectrum is not normal, the position of the spectral lines is not exactly proportional to the wave length. Theoretically, the correction curve rectifies this difficulty.

(2) The true focal curve and the theoretical curve of the plate are usually not the same. There is often a slight error remaining even after a great deal of mechanical adjusting.

(3) The spectrogram may be inclined to the focal plane.

(4) A curvature of the spectral lines occurs on the plate. It is a function of the angle of incidence between the slit and the normal to the grating.

(5) The photographic emulsion does not shrink evenly.

(6) Great care was taken to keep the temperature and pressure of the hydrogen and of the air between the slit, grating, and plate constant. Any change in these would have introduced a large error.

(7) Very small amounts of impurities are readily detectable in the electrodes of the Pfund arc. However, since only those lines which corresponded to Mrs. Clancy's lines were included in this thesis, the wave lengths of impurities should not affect the recorded lines. There is the possibility

that strong lines of impurities have obscured hydrogen lines in the immediate vicinity.

(8) There is a very slight possibility of error due to the microdensitometer. There is a negligible backlash and no important change with temperature. The average deviation of the automatic recorder is 0.0003Å.

(9) The secondary iron standards chosen had values occuring in both M.I.T. tables and Dr. Combes' thesis. Since Dr. Combes used these secondary standards to determine his tertiary hydrogen standards, the latter should have an average deviation of 0.001 Å.

(10) The actual drawing of the correction curve is accurate to 0.001 Å. No attempt was made to read it beyond thousandths of an Angstrom.

(11) The wide hydrogen lines are so intense that the wave lengths recorded on the two film vary greatly. The two film read opposite sides of the intensity peaks. Hence the wave lengths are less accurate for wide lines.

(12) Increase in temperature or pressure cause a broadening of spectral lines and thus decrease the accuracy of their determination. The width of the line on the plate is also a function of slit width, minimum width being limited by diffraction effects. (See Statement on page 46).

The fairly constant deviation between the two film of from approximately 0.01 Å to 0.03 Å is taken care of when the film averages are corrected by the graph.

Combining the above errors, the determination of the wave lengths can not be accurate to less than 0.02 Å.

WIDTH OF THE SPECTRAL LINES

The natural width of the spectral line may be determined from a distribution curve obtained by plotting the intensity of radiation against the wave length for each line. Collisions of radiating atoms with other atoms result in a broadening of the spectral line. The Doppler effect also causes broadening of spectral lines. The radiating atom approaching the observer emits a shorter wave length than a stationary atom, and the receding atom emits a longer wave length. Increase in temperature or pressure increases the number of collisions and the motion of the atoms, and hence increases the width of the spectral lines. The slit width and consequently the spectral line width is limited by diffraction effects.

BIBLIOGRAPHY

Mrs. E.B. Clancy, Master's Thesis Boston University, 1946 The Computation of Wave Lengths of Molecular Hydrogen Between 5145 and 5810

L.S. Combes, Ph.D. Dissertation Boston University, 1939 Interferometer Method of Determining Wave Lengths in the Hydrogen Spectrum

A. C. Hardy and F.H. Perrin, The Principle of Optics, McGraw-Hill, 1932

G.R. Harrison, Massachusetts Institute of Technology Wavelength Tables, John Wiley & Sons, 1939

Gerhard Herzberg, Atomic Spectra and Atomic Structure, Prentice-Hall, 1937

Gerhard Herzberg, Molecular Spectra and Molecular Structure, Prentice-Hall, 1939

F.A.Jenkins and H.E.White, Fundamentals of Physical Optics, McGraw-Hill, 1937

N.A.Kent and R.G.Lacount, Physical Review 51, 241 (1937)

R.G.Lacount, Ph.D. Dissertation Boston University, 1935 Interferometer Determinations of Certain Wave Lengths

O.W.Richardson, Molecular Hydrogen and Its Spectrum, Yale University Press, 1934

H.N.Russell and C.E.Moore, Transactions of the American Philosophical Society 34, Part II (1944)

R.A.Sawyer, Experimental Spectroscopy, Prentice-Hall, 1944

Henry Semat, Introduction to Atomic Physics, Farrar & Rinehart, 1939

H.W. Thompson, A Course in Chemical Spectroscopy, Clarendon Press, 1938

ABSTRACT

This paper presents the wave lengths of molecular hydrogen spectrum in the region 5200 Å to 5800 Å as determined by measurement and comparison with iron and previously determined molecular hydrogen lines.

Dr. R. G. Lacount obtained a spectrogram of hydrogen and iron lines in this region by exposing a plate in a Littrow-mount spectrograph at Boston University using a hydrogen discharge tube and a Pfund arc as sources.

The wave lengths and intensities of the spectrogram lines were measured with the Harrison automatic recorder in the direction of (1) increasing and (2) decreasing wave length.

Corrections were added to the average values. A correction curve was drawn through points plotted for a series of secondary iron standards and tertiary hydrogen standards. The average film values for these standard lines were plotted as abscissa and the differences between the film and the true standard lines plotted as ordinates.

The averaged corrected values were then compared with M.I.T. iron tables and those published by H.N.Russell in Transactions of the American Philosophical Society, Volume 34, and also with hydrogen lines in Mrs. Clancy's master's thesis. In most cases only those lines agreeing within 0.1 Å with Mrs. Clancy's lines were recorded. Many of the latter writer's lines did not appear on the films because of intense iron

lines in the vicinity or lines due to impurities.

The line intensity traces made by the microphotometer were recorded on a scale from 0 - 8. The intensities did not enter into calculations, but are recorded since estimates of transition probabilities may be made from them.

Table II contains the results of the investigation made of the hydrogen molecular spectrum in the region 5200 to λ5800. It includes

Approximately measured values of intensities.

Wave lengths in both the direction of increasing and decreasing wave length.

Average wave length values to seven significant figures.

Corrections interpolated from the correction curve for each line appearing on both films.

Averaged corrected wave lengths to seven significant figures.

Wave numbers in air, the reciprocals of the wave lengths.