

I wish to express my thanks for the interest Professor H. S. Taylor and Professor K. T. Compton have taken in this derivation.

<sup>1</sup> Wien's Displacement Law is proved by thermodynamic considerations and by experiment in contradistinction to Wien's Radiation Formula, which is only proved experimentally for small values of  $\lambda$ .

<sup>2</sup> Coblenz, W. W., *Bur. Standards Scient. Pap.*, No. 406 (1920).

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CRITICAL POTENTIALS AND THE HEAT OF DISSOCIATION  
OF HYDROGEN AS DETERMINED FROM ITS ULTRA-VIOLET  
BAND SPECTRUM

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Lyman has found that under certain conditions of excitation the mixture of small proportions of hydrogen with argon causes the former to emit a series of eleven groups of lines, lying between  $\lambda\lambda$  1063 and 1670. Five of these groups he mentions in his book, "The Spectroscopy of the Extreme Ultra-Violet" (pp. 79-81), the others he discovered more recently. As shown in figure 1, which is a reproduction of one of Lyman's plates, these groups are at approximately equal intervals on a wave-length scale, except that one group is missing or very faint. Subsequently in studying and measuring Lyman's plates another group was found at the long wave-length end of the series. This group is very faint and has only two lines, whereas all the other groups have at least five or six each. If we number the groups 0, 1, 2, etc., beginning with the group of shortest wave-length and include the missing group, the faint group at the other end of the series is group 12 and the group that is missing or very faint is group 3. The zero group is partly obscured by one of the two extremely intense argon lines corresponding to its resonance potential of 11.6 volts. The other argon line is on the short wave-length side of this group.

The analysis made by the writer indicates that these groups constitute a one-dimensional series of bands, which have a common vibrational state in the upper level. We shall designate these bands the Lyman bands of hydrogen. They are degraded toward the red, and are apparently *Q* branches with perturbations near the origin. The one-dimensional character of the series seems to have the following explanation. Under the conditions of excitation the energy imparted to a hydrogen molecule is limited to 11.6 volts, the resonance potential of argon. This is just sufficient to raise the hydrogen molecule from the normal level with zero

vibrational energy to the first excited electronic level with zero vibrational energy. For the sake of convenience we shall introduce  $e_i$  for the total electronic quantum number in the sense in which this nomenclature is used in atomic spectra, and as usual designate by  $n$  and  $m$  the vibrational and nuclear rotational quantum numbers respectively. In this terminology we shall describe the process of excitation as raising the molecule from the state  $e_i = 1, n = 0$  to the state  $e_i = 2, n = 0$ . The justification for this particular assignment of total electronic quantum numbers will be given later. The transitions made by the molecule in returning to lower levels are  $e_i' = 2, n' = 0$  to  $e_i'' = 1, n'' = 0$  to 12. According to the experimental results of Mulliken<sup>1</sup> and the theoretical results stated in a recent paper by Born and Jordan<sup>2</sup> half-integers should be used for the vibrational quantum numbers, but for the sake of convenience integers half a unit lower than the true vibrational quantum numbers are used in this discussion.

In the preceding explanation it has been found necessary to assume that the energy imparted to a hydrogen molecule is limited to 11.6 volts. Since these bands were excited by an electrical discharge such as occurs in an ordinary discharge tube, and not by a stream of electrons of uniform velocity, this limitation of the energy itself requires an explanation. There are two possible causes, both of which are presumably operative at the same time. One is the excitation of hydrogen molecules by collisions of the second kind with excited argon atoms having an energy of 11.6 volts. The other is that the presence of the argon limits the velocity of the free electrons to 11.6 volts, its lowest resonance potential, since electrons with greater velocity would suffer inelastic impact with argon atoms and lose their energy. This explanation would seem to be in accord with the experimentally observed fact that a large proportion of argon is required in the mixture in order to bring out this simple series of bands to the exclusion of the rest of the secondary spectrum in the extreme ultraviolet.

Designating by  $E$  the vibrational energy in the lower or normal level, the curve  $\left(n'', \frac{1}{h} \frac{\Delta E}{\Delta n''}\right)$  for these bands indicates that  $\frac{dE}{dn''}$ , which is a measure of the vibrational frequency, becomes zero shortly beyond  $n'' = 12$ , so that at  $n'' = 12$  the molecule is on the verge of dissociation, and apparently  $n'' = 13$  cannot exist. Evidently the heat of dissociation,  $D$ , of the hydrogen molecule is equal to the vibrational energy for that value of  $n''$  at which the frequency is zero. The data permit the computation of this quantity with a fair degree of accuracy. The computations yield 4.22 volts or 97,350 calories as the lower limit of the value of  $D$ , and 4.375 volts or 101,000 calories as the upper limit of  $D$ . Finally, using a power series representation of  $E$  as function of  $n''$ , it was found that

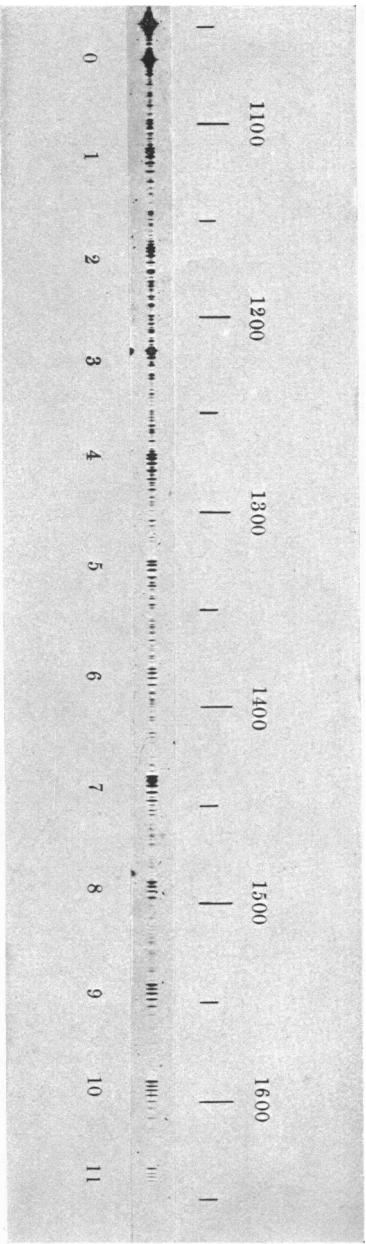
$$\frac{dE}{dn''} = 0 \text{ for } n'' = 12.86,$$

$$\begin{aligned} \text{and } D &= E(12.86) = 4.27 \text{ volts} \\ &= 98,570 \text{ calories.} \end{aligned}$$

This value of  $D$ , in the opinion of the writer, is not in error by more than 0.05 volt. It agrees with Isnardi's<sup>3</sup> result (as corrected by Wohl) that  $D$  lies between 96,765 and 102,257 calories. The value obtained by Langmuir<sup>4</sup> was 84,000 calories.

Other constants of the hydrogen molecule obtained from our data are: the lowest resonance potential = 11.61 volts; the frequency of infinitesimal vibration  $\omega_0$  in the normal state = 4260.cm.<sup>-1</sup>, which is in fair agreement with the value 4880.cm.<sup>-1</sup>, obtained by Kemble and Van Vleck<sup>5</sup> from specific heat data; and the value of  $\chi\omega_0$  (coefficient of  $n^2$ ) for the normal state = 112.5. cm.<sup>-1</sup>.

The introduction of total electronic quantum numbers will now be discussed. Sommerfeld<sup>6</sup> refers to the ultra-violet band spectrum of hydrogen as holding the same relationship to the visible band spectrum that the Lyman series does to the Balmer series. Furthermore, the diagram due to Glitscher in the fourth and earlier editions of Sommerfeld's "Atombau und Spektrallinien" shows that even in the visible there is a close parallelism between the band spectrum and the Balmer series. This seems to indicate that the hydrogen molecule has approximately the same series of electronic energy levels as the hydrogen atom, and that it is possible to assign total electronic quantum numbers to the orbits of the radiating electron of the molecule in such a way that the difference in energy of two orbits of total quantum numbers  $e_i'$  and  $e_i''$  will be nearly the same as the difference in energy of the orbits of the same total quantum numbers in the hydrogen atom. The energy of corresponding orbits is not the same, however. In the Glitscher diagram it will be observed that the peaks  $\alpha, \beta, \gamma, \delta$  are all on the short wave-length side of the corresponding lines of the Balmer series. This is in accord with the fact that the lowest resonance potential and the ionization potential of the molecule are each higher than the corresponding potentials of the atoms. All this shows that the electron in the  $n$ th quantum orbit in the molecule is more tightly bound than the electron in the  $n$ th quantum orbit in the atom. On the basis of this parallelism the lowest resonance potential of the molecule, which we found to be 11.61 volts, must correspond to 10.15 volts, the lowest resonance potential of the atom, and must be due to the electronic transition  $e_i = 2$  to  $e_i = 1$ . This accounts for our previous assignment of total electronic quantum numbers. According to this scheme the ultra-violet band spectrum is due to the electronic transitions,  $e_i' \gg 2$  to  $e_i'' =$



1, while the visible band spectrum is due to the electronic transitions,  $e_i'' \gg 3$  to  $e_i' = 2$ .

On this theoretical basis an attempt will now be made to compute the higher resonance potentials and the ionization potential of the hydrogen molecule, using the Glitscher diagram. Let us assume that the peaks marked  $\alpha, \beta, \gamma, \delta$  on the Glitscher diagram represent electronic transitions corresponding to the electronic transitions of the hydrogen atom that cause the emission of the lines  $\alpha, \beta, \gamma, \delta$ , respectively, of the Balmer series. In other words these peaks represent the location of the (0, 0) bands for the corresponding electronic transitions. On this assumption by adding the voltage corresponding to each of these peaks to 11.61 volts one should obtain the higher resonance potentials of the molecule and by extrapolation the ionization potential. This is done below. The values of  $\nu$  in table 1 are taken from the Glitscher diagram.

PEAK	$\nu$	$V = 1.2344 \times 10^{-4}$
$\alpha$	16,650 cm. <sup>-1</sup>	2.055 volts
$\beta$	21,850	2.697
$\gamma$	24,500	3.030
$\delta$	25,900	3.197

$e_i$	CRITICAL POTENTIALS	
	$V$	$V(\text{calc})$
2	11.61 volts	11.610 volts
3	13.665	13.631
4	14.31	14.323
5	14.64	14.639
6	14.81	14.810
$\infty$	15.19	15.193

The critical potentials corresponding to jumps from the orbit  $e_i = 1$  to higher orbits are given table 2. In the second column under  $V$  are given the values obtained by adding the voltages in table 1 to 11.61 volts. The value for  $e_i = \infty$  was obtained by extrapolation. The theoretical discussion above as well as previous work of Fowler<sup>7</sup> and Sporer<sup>8</sup> suggested using a Rydberg formula to represent this series of values of  $V$ . The last column under  $V(\text{calc})$  was computed from the Rydberg formula

$$V = 13.539 \left\{ \frac{1}{(1-\alpha)^2} - \frac{1}{(e_i-\alpha)^2} \right\}$$

with  $\alpha = 0.0560$ . It will be observed that this Rydberg formula gives a remarkably good representation of this series of values of  $V$ . Furthermore, even though the values obtained by the use of the Glitscher diagram be regarded as doubtful, still the value of 11.61 volts as the lowest reso-

nance potential would have yielded the series of values under  $V(\text{calc})$ . For we might have found  $\alpha$  by solving the equation

$$11.61 = 13.539 \left\{ \frac{1}{(1-\alpha)^2} - \frac{1}{(2-\alpha)^2} \right\},$$

which, of course, gives  $\alpha = 0.0560$ , and therefore the previous values of  $V(\text{calc})$ .

While the azimuthal quantum numbers have not been considered in the preceding discussion, it seems natural to suppose that it will be necessary to introduce them in addition to the total electronic quantum numbers in order to define the electronic energy levels of the hydrogen molecule. If such is the case, there are two potentials corresponding to  $e_i = 2$ . The lower one of these, we know, is 11.61 volts. Consequently the other one must be higher. Now it may be that, in spite of the numerical agreement indicated in table 2, it is the higher of these two potentials that is related to the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  peaks in the Glitscher diagram, and that instead of a Rydberg formula, we should use a Ritz formula. This would raise the value of the ionization potential, but probably not more than a few tenths of a volt.

Although the analysis of the secondary spectrum has not progressed to the point where one can make an accurate computation of the ionization potential of the molecule, nevertheless we may conclude that the spectroscopic data considered yield 15.19 volts as the probable value of that constant. It is possible that further investigation will raise this value several tenths of a volt, but it certainly does not seem as though the spectroscopic data would yield a value as high as the average obtained from electron impact experiments.

This apparent lack of agreement between the spectroscopic and the experimental values does not necessarily indicate that one or the other is wrong. For, according to recent work of Franck<sup>9</sup> and Birge and Sponer,<sup>10</sup> if an electronic transition causes a considerable change in the moment of inertia of a molecule, then it will not be possible in general to raise the electron from the lower to the higher level without exciting a certain minimum of vibrational energy. Where the excitation is by electron impact this energy must come from the impacting electron. It follows, therefore, that the minimum energy of an impacting electron required to produce a given electronic transition in the molecule will be equal to the difference in energy of the electronic levels in question plus the minimum vibrational energy excited by the electronic transition. This, of course, applies not only to the process of excitation, but to ionization also. It must, therefore, be expected that in these cases the observed critical potentials will be higher than the spectroscopic data would indicate.

In the case of hydrogen, the value of  $C$ , the coefficient of  $m^2$ , for the Lyman bands indicates that there is an extremely large change in the moment of inertia in going from the normal level to the first excited level. It is, therefore, highly probable that large changes in the moment of inertia occur when the electron is raised from the normal level to any higher level or when ionization occurs. If this assumption is correct, one would expect the observed critical potentials of the hydrogen molecule to be higher than those obtained from the spectroscopic data. This would account for the difference between the value of the ionization potential, 15.19 volts, obtained above and the value obtained from electron impact experiments.

If  $I_a$  is the ionization potential of the atom of an element,  $I_m$  that of its diatomic molecule,  $D$  the heat of dissociation of the neutral molecule, and  $D'$  that of the ionized molecule, it can easily be shown<sup>11</sup> that

$$I_a + D = I_m + D'$$

For hydrogen  $I_a + D = 13.54 + 4.27 = 17.81$  volts.

If we take  $I_m = 15.19$  volts,

$$D' = 2.62 \text{ volts.}$$

Urey's<sup>12</sup> theoretical value of  $D'$  is 3.12 volts. Sommerfeld,<sup>13</sup> on the other hand, assumes that  $D = I_m - I_a$ , which automatically makes  $D' = 0$ . The data from positive ray analysis<sup>14</sup> shows that  $H^+$  and  $H_3^+$  appear at the same voltage as  $H_2^+$ . At low pressures ( $H^+ + H_3^+$ ) forms only a small percentage of the total number of ions, but as the pressure increases the percentage of these ions increases also. This has been interpreted to indicate that the stability of  $H_2^+$  is small or zero. In view of the fact that the energy with which the ions collide after their formation in the apparatus is unknown, this evidence must be considered inconclusive. Furthermore, according to the conclusions of the preceding paragraph, the ionized molecules produced in a positive ray apparatus will have considerable vibrational energy when formed. Therefore, unless they lose their energy in the meantime, it will require somewhat less than 2.62 volts to complete dissociation. Thus, if we assume the observed ionization potential to be 15.8 volts, the ionized molecules will have 0.6 volt of vibrational energy when formed and will require only 2.02 volts to complete dissociation.

The writer wishes to express his thanks to Prof. T. Lyman, who obtained the spectrum plates used in this investigation, and to Prof. E. C. Kemble and Dr. R. S. Mulliken, whose criticism and suggestions have been of great value.

*Note added in proof:* Since this paper was written, it has been found that the two lines supposed to constitute group 12 are due to impurities. With this change in the data, the lower limit of the heat of dissociation,  $D$ , of the hydrogen molecule becomes 4.10 volts or 94,600 calories, the upper limit 4.50 volts or 103,800 calories and the probable value of  $D$  4.34 volts or 100,100 calories.

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<sup>1</sup> Mulliken, *Physic. Rev.*, **25**, 119, 1925.

<sup>2</sup> Born and Jordan, *Zeit. Physik.*, **34**, 858, 1925.

<sup>3</sup> Isnardi, *Zeit. Elektrochemie*, **21**, 405, 1915. Wohl (*Ibid.*, **30**, 49, 1924) corrected a slight error in computation in Isnardi's work, thereby raising his value about 5000 calories.

<sup>4</sup> Langmuir, *J. Amer. Chem. Soc.*, **37**, 417, 1915.

<sup>5</sup> Kemble and Van Vleck, *Physic. Rev.*, **21**, 653, 1923.

<sup>6</sup> Sommerfeld, *Atombau und Spektrallinien*, pp. 519-520.

<sup>7</sup> Fowler, *Proc. Roy. Soc.*, A **91**, 208, 1915.

<sup>8</sup> Sponer, *Zeit. Physik.*, **34**, 622, 1925.

<sup>9</sup> Franck, *Trans. Faraday Society*, 1925.

<sup>10</sup> Birge and Sponer, unpublished work.

<sup>11</sup> Cf. Birge and Sponer, abstract 18, and Birge, abstract 19, March, 1926, meeting, Amer. Phys. Soc.

<sup>12</sup> Urey, *Physic. Rev.*, **27**, 216, 1926.

<sup>13</sup> Sommerfeld, *Atombau und Spektrallinien*, p. 518.

<sup>14</sup> Smyth, *Physic. Rev.*, **25**, 452, 1925; Hogness and Lunn, *Ibid.*, **26**, 44, 1925.

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## CURVED SPACE-TIME AND RADIATION

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1. Nearly two years ago, studying electrodynamics in curved space-time I found<sup>1</sup> that Maxwell's equations impose on space-time a restriction which can be formulated by saying that a certain vector  $q$  determined by the curvature field must be the gradient of a scalar function, or

$$\text{Rot } q = 0. \tag{1}$$

It also was shown at that time<sup>2</sup> that the expression for the electromagnetic tensor involves the function  $\varphi$ , of which  $q$  is the gradient, under the sin and cos signs so that if, under separation of time and space at a certain point, the time component  $q_t$  of  $q$  does not change with time the electric and magnetic forces at that point are periodic functions of time, the period being  $2\pi/q_t$ ; we have what would seem to be monochromatic light of frequency  $q_t/2\pi$ .

It is important to note that in these statements the term periodicity does not involve the assumption that the phenomenon occupies a time interval greater than the period; it is applicable to any interval of time however small.

2. During the last two years I made several attempts to find some simple