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CRITICAL POTENTIALS AND THE HEAT OF DISSOCIATION OF HYDROGEN AS DETERMINED FROM ITS ULTRA-VIOLET BAND SPECTRUM[1]

By Enos E. Witmer*

Abstract

Lyman has found that if a tube containing argon with a trace of hydrogen is excited by an uncondensed discharge, a simple spectrum is obtained that consists of twelve groups of lines of the secondary spectrum in the extreme ultraviolet. The group of shortest wave-length is partly obscured by one of the two extremely intense lines of argon, that correspond to its resonance potentials of 11.57 and 11.78 volts. The present investigation has shown that these groups are *bands,* due to the transitions from a single electronic and vibrational state, A, $n'=a$ to the electronic and vibrational states N, $n''=0$ to 11. These bands are apparently Q branches with perturbations near the origin. The first lines fit the empirical formula

$$\nu=94075-4267\,n''+113.5\,n''^2+\cdots$$

The existance of a definite upper state is due to the argon, which, acting through *limitation of electron velocities* and *collisions of the second kind,* limits the energy that can be imparted to a hydrogen molecule to 11.78 volts. This is just sufficient to raise the molecule from the normal state N, $n=0$ to the excited state A, $n=a$. If $a=0$, the radiation potential for these bands is 11.61 volts, which agrees with the experimental values of the lowest radiation potential of the hydrogen molecule. The data permit the computation of the *heat of dissociation, D,* of the hydrogen molecule. The lower limit of D is 4.10 volts or 94,600 calories per mol, and the upper limit 4.56 volts or 105,200 calories. The probable value is 4.34 volts or 100,100 calories. This is in agreement with the best experimental values.

There is a remarkable parallelism between the atomic and molecular spectra of hydrogen, that seems to indicate that the electronic energy levels in the two cases must be very similar. An attempt was therefore made to introduce *total electronic quantum numbers,* e_t, and to compute the higher *critical potentials* of the hydrogen molecule. To the electronic level N was assigned the value $e_t=1$, and to the level A the value $e_t=2$. The ultra-violet band spectrum is due to the transitions $e_t\geqq 2$ to $e_t=1$, and the visible spectrum to the transitions $e_t\geqq 3$ to $e_t=2$. The higher critical potentials were computed by two methods, first, by use of the Glitscher diagram (in Sommerfeld's Atombau), and, secondly, by use of a Rydberg formula. The remarkable agreement between the values obtained by the two methods seems to indicate that these values have some significance. These values are 13.64, 14.32, 14.64, 14.81 volts, etc., giving an ionization potential of 15.19 volts. Several suggestions are made concerning the discrepancy between this value and the experimental values.

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[1] E. E. Witmer, Phys. Rev. **27,** 513 (Abstract) (1926). Proc. Nat. Acad. Sci. **12,** 238–244 (1926).

The *heat of dissociation of the ionized hydrogen molecule* is also obtained. Using our value of the ionization potential of H_2, its value is 2.69 volts. A suggestion is also made concerning the vibrational quantum numbers of the Fulcher Bands. *Other bands* due to the electronic transition A to N were also found and assigned vibrational quantum numbers.

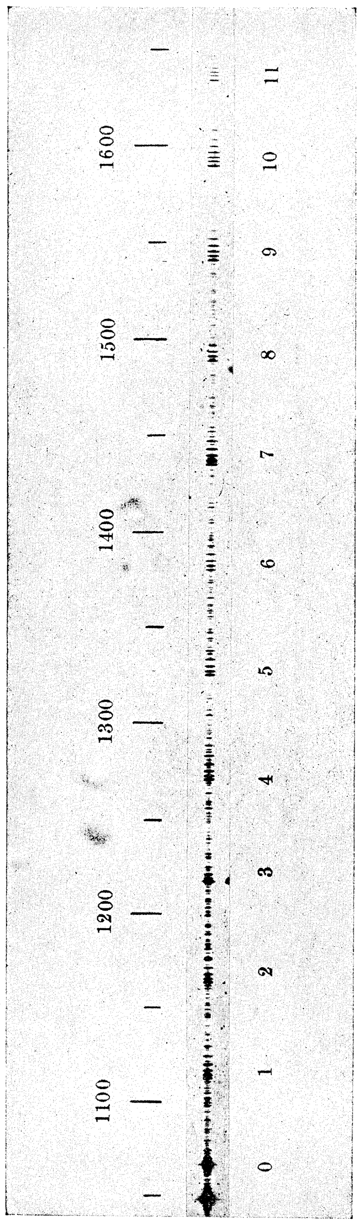

Fig. 1. The Lyman Bands.

THE secondary spectrum of hydrogen is a band spectrum emitted by molecular hydrogen. On account of the small moment of inertia of the hydrogen molecule, however, this spectrum does not have the appearance of an ordinary band spectrum, but rather that of a very rich line spectrum, so that in most cases it is impossible to pick out by mere inspection the lines that belong together in a single band. For this reason it is a very difficult spectrum to analyze without physical methods to assist in determining the correct grouping of the lines. Fortunately it was discovered by Professor Lyman some years ago that under certain conditions of excitation the mixture of small proportions of hydrogen with argon causes the former to emit in the extreme ultra-violet a spectrum very much simpler than the complete secondary spectrum in that region. This spectrum consists of a series of twelve groups of lines. Five of these groups he mentions in his book,[2] "The Spectroscopy of the Extreme Ultra-Violet"; the remaining groups he found on plates taken in May, 1925. The investigation of this spectrum was suggested by Professor Lyman, and the work reported in this paper is based on a study and measurement of his last plates, which were kindly placed at the writer's disposal.

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[2] T. Lyman, Spectroscopy of the Extreme Ultra-Violet, pp. 74–81, also Table I in the Appendix.

Fig. 1 is a reproduction of this spectrum with a wave-length scale. The groups have been numbered 0, 1, 2, 3, etc., beginning with the group of shortest wave-length. The zero group is partly obscured by one of the two extremely intense resonance lines of argon, λλ1048.26 and 1066.71, and group 3 is very much fainter than the other groups. The general appearance of the spectrum is that of a one-dimensional series of bands degraded toward the red. The usual second difference test confirms this conclusion. These bands will be referred to hereafter as the Lyman bands.

Practically all the intense lines of this spectrum in the region λλ1230 to 1650 have been identified with lines of the secondary spectrum in Lyman's[2] table. Some of the remaining lines have also been identified on plates of the complete secondary spectrum. Since the numerical relationships show that all the lines belong together, there can be no doubt that the complete spectrum is part of the secondary spectrum.

In measuring these plates the lines of atomic hydrogen have been used as fiducial lines. The first three lines of the Lyman series occur on all these plates, the first two being very intense. In addition to these lines there were available for use as checks the oxygen triplet[3] at λ1302.27, argon lines measured by Professor Saunders, and in one case the third line of the Lyman series in the second order.

In Table I are given the measurements on this spectrum. m denotes the rotational quantum number provisionally assigned to the lines of each band, λ and ν being as usual wave-length in Ångstroms and wave-number respectively. In Band 0 three lines were obscured by the extremely intense argon line λ1066.71, and in Band 3, which is very faint two lines at the head were obscured by the intense line λ1215.68 of atomic hydrogen. The probable values of these missing lines have been inserted in parentheses to complete the table. The wave-lengths given in the table are, with a few exceptions as in the case of faint lines, the average of three or more independent measurements. The greatest deviation from the mean is in every case equal to or less than .20A°.

Assuming the applicability of the well known formula

$$\nu = A + 2Bm + Cm^2 \tag{1}$$

for the lines of a band, it follows that the second differences should be equal to the constant, $2C$. While there is considerable deviation from constancy in the second differences in Table I, the regularities are sufficient to demonstrate the band character of these groups. Many of the smaller irregularities are probably due to experimental errors in the

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[3] J. J. Hopfield and S. W. Leifson, Astrophys. J. **58,** 61 (1923)

wave-lengths; the larger irregularities are real as shown by their constant appearance in all sets of measurements. There is no doubt, for example, that in bands 4–11 inclusive there are irregularities about the head, and that approximately constant second differences are obtained in these cases only if the first two lines be omitted in forming the differences.

TABLE I

The Lyman Bands

m	Intensity	λ	ν	Differences 1st	Differences 2nd
		Band 0			
1	4	1062.98	94 075		
				(47)	
2		(1063.51)	(94 028)		(66)
				(113)	
3		(1064.79)	(93 915)		(83)
				(196)	
4		(1067.02)	(93 719)		(83)
				(279)	
5	5	1070.21	93 440		(83)
				362	
6	4	1074.37	93 078		79
				441	
7	1	1079.48	92 637		
			Ave.		78.8
		Band 1			
1	8	1112.08	89 922		
				46	
2	8	1112.64	89 876		66
				112	
3	10	1114.03	89 764		75
				187	
4	10	1116.36	89 577		76
				263	
5	9	1119.64	89 314		78
				341	
6	8	1123.94	88 973		68
				409	
7	2	1129.13	88 564		
			Ave.		72.6
		Band 2			
1	8	1162.88	85 993		
				38	
2	8	1163.40	85 955		71
				109	
3	10	1164.87	85 846		65
				174	
4	10	1167.24	85 672		74
				248	
5	10	1170.63	85 424		66
				314	
6	8	1174.95	85 110		76
				390	
7	1	1180.36	84 720		
			Ave.		70.4
		Band 3			
1		(1215.02)	(82 303)		
				(45)	
2		(1215.68)	(82 258)		(60)
				(105)	
3	2	1217.24	82 153		(49)
				154	
4	2	1219.52	81 999		82
				236	
5	2	1223.04	81 763		56
				292	
6	0	1227.43	81 471		
			Ave.		61.7
		Band 4			
1	8	1268.52	78 832		
				24	
2	8	1268.90	78 808		81
				105	
3	10	1270.60	78 703		53
				158	
4	10	1273.15	78 545		57
				215	
5	10	1276.65	78 330		59
				274	
6	8	1281.13	78 056		51
				325	
7	0	1286.49	77 731		
		Ave. (excluding first value)			55.0
		Band 5			
1	10 *	1322.96	75 588–		
				15	
2		1323.22	75 573–		
	10 *	1324.64	75 492		
				107–	
3		1325.07	75 466–		40
				147–	
4	10	1327.69	75 319–		51
				198–	
5	9	1331.18	75 121–		54
				252–	
6	5	1335.66	74 869–		38
				290–	
7	0	1340.86	74 579–		
			Ave.		45.8

*These doublets were not resolved sufficiently for accurate measurement.

TABLE I (*Continued*)

The Layman Bands

m	Intensity	λ	ν	Difference 1st	Difference 2nd
		Band 6			
1	6	1377.99	72 569		
				108	
3	7	1380.05	72 461		
				132	
4	8	1382.58	72 329		51
				183	
5	8	1386.07	72 146		43
				226	
6	1	1390.44	71 920		
			Ave.		47.0
		Band 7†			
1	10	1432.83	69 792–		
	4	1434.11	69 730	109	
3	10	1435.08	69 683–		
	1	1436.11	69 633	121–	
4	10	1437.57	69 562–		44
				165–	
5	10	1440.98	69 397–		36
				201–	
6	8	1445.18	69 196–		40
				241–	
7	1	1450.22	68 955–		
			Ave.		40.0
		Band 8			
1	5	1486.97	67 251		
				44	
2	0	1487.93	67 207		16
				60	
3	4	1489.26	67 147		47
				107	
4	4	1491.65	67 040		40
				147	
5	3	1494.93	66 893		27
				174	
6	0	1498.82	66 719		
			Ave.		32.5

m	Intensity	λ	ν	Differences 1st	Differences 2nd
		Band 9			
1	6	1539.36	64 962		
				24	
2	1	1539.92	64 938		
				76	
3	6	1541.74	64 862		22
				98	
4	6	1544.07	64 764		28
				126	
5	6	1547.07	64 638		26
				152	
6	2	1550.73	64 486		26
				178	
7	0	1555.01	64 308		
			Ave.		25.5
		Band 10			
1	10	1588.92	62 936		
				48	
2	1	1590.12	62 888		
				49	
3	10	1591.38	62 839		
				82	
4	10	1593.46	62 757		22
				104	
5	10	1596.10	62 653		17
				121	
6	4	1599.19	62 532		23
				144	
7	0	1602.87	62 388		
			Ave.		20.7
		Band 11			
1	3	1633.65	61 213		
				15	
2	3	1634.03	61 198		
				87	
3	4	1636.36	61 111		
				66	
4	4	1638.14	61 045		15
				81	
5	3	1640.32	60 964		13
				94	
6	0	1642.84	60 870		
			Ave.		14.0

The values of C obtained from Table I, though not very accurate, yield the empirical equation

$$C = -(40-3p) \tag{2}$$

where p is the number of the band. This is an extremely large value of C. It shows that there is a very large increase in the moment of inertia of

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†There are two lines that by all indications belong to this group, but which do not fit into the scheme.

the hydrogen molecule in going from the lower to the upper of the two electronic states involved in the emission of these bands.

Bands 1 and 2 are apparently Q branches without perturbations. Fig. 2 is a Fortrat diagram of band 1. The remaining bands from 4–11 inclusive can be fitted to parabolic curves in which the second line is usually faint or displaced or both. An example is Fig. 3, which is a diagram of band 11. It will be observed that in this diagram the angle of intersection between the parabola and the ν axis is not quite a right angle, but an acute angle (if one uses the angle in which the parabola lies). This is true of all the bands from 6–11 inclusive and possibly of some of the others. If, however, the outer lines 3, 4, 5, etc. of any band be used to compute the constants of the parabola, it is found that the computed head in all cases falls within 20 or 30 cm^{-1} of the first observed line. On the whole these bands fit into the category of Q branches better than any other.

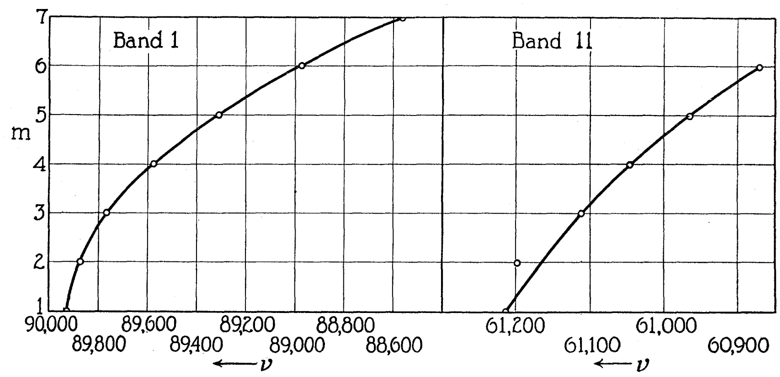

Fig. 2. Fortrat diagram of Lyman band No. 1.
Fig. 3. Fortrat diagram of Lyman band No. 11.

The frequencies of the origin of the bands in any given system are given by the well known formula

$$\nu=\nu_e+n'\omega_0'(1-x'n'+\cdots)-n''\omega_0(1-x''n''+\cdots), \qquad (3)$$

where the primed letters refer to the initial state in emission and the doubly primed letters to the final state,† n being the vibrational quantum number. In this case the frequencies of the first lines of the bands fit the empirical formula

$$\nu=94\ 075-4267p+113.5p^2+\cdots \qquad (4)$$

If these are Q branches, as we suppose, the first line of each band will

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†Throughout this paper primed letters refer to the initial state in emission and doubly primed letters to the final state.

lie very close to the origin and we may proceed to identify (3) and (4). Since x in Eq. (3) is positive, almost without exception, it follows that in Eq. (4) the variable part of the left-hand member is a function of n'' rather than n'. For no permissible transformation can change the sign of the coefficient of p^2. This shows that the initial state is constant and the final state variable. It seems highly probable, therefore, that the band of shortest wave-length would have the value $n''=0$, thus making $p=n''$. If in accord with the experimental results of Mulliken[4] and the theoretical results stated by Born and Jordan[5] half-integral vibrational quantum numbers were used, then $n''=p+\frac{1}{2}$. In this paper the integral values will be used for the sake of convenience.

The lower electronic level involved in the emission of these bands will be designated N, and the upper level A.

Mode of Excitation

Lyman[2] describes in detail the conditions under which these bands are emitted to the exclusion of the rest of the secondary spectrum in the extreme ultra-violet. The two essential conditions are that the argon contain only a small proportion of hydrogen and that the discharge be uncondensed. That the argon plays an important rôle is shown, furthermore, by the fact that the head of the zero band lies between the two extremely intense resonance lines of argon, λλ1048.26 and 1066.71. The corresponding resonance potentials are 11.78 and 11.57 volts, while the potential corresponding to the head of the zero band is 11.61 volts. These facts seem to indicate that the lower electronic level N is the normal level of the hydrogen molecule, and that due to the presence of the argon, almost all the excited hydrogen molecules exist in the one electronic and vibrational state A, $n=a$, where a is some definite integer, as yet unknown.

Let us consider in detail the probable conditions in the tube in which these bands are excited. Since the argon is far in excess of the hydrogen, the argon will determine the velocity distribution of the free electrons. The general nature of this distribution must be something like that indicated in Fig. 4. There will be many electrons per volt of velocity below the lowest resonance potential, 11.57 volts, and big drops in the number per volt both at this point and at 11.78 volts. A very large number of the argon atoms will be in these two resonance states.

The hydrogen molecules are initially in the normal electronic state, which will be assumed to be N. The further assumption will be made

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[4] R. S. Milliken, Phys. Rev. **25**, 119 (1925).

[5] M. Born and P. Jordan, Zeits. f. Physik. **34**, 858 (1925).

that almost all the hydrogen molecules in this electronic state are in the vibrational state $n=0$. Using the Boltzmann formula, a simple computation shows that even at 1000°K under conditions of thermal equilibrium the number of molecules in the state N, $n=1$ would be only 0.26 percent of the number in the state N, $n=0$; and, while it cannot be assumed that a temperature distribution prevails in a discharge tube, it is at least not unreasonable to suppose that the percentage of molecules in higher vibrational states was in this particular case quite small.

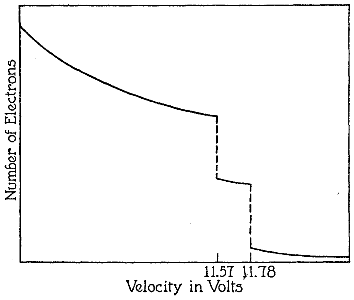

Fig. 4. Diagram showing the probable velocity distribution of the electrons in the discharge tube producing the Lyman bands. 11.57 and 11.78 volts are the resonance potentials of argon.

The hydrogen molecules may be excited by two processes, by collisions of the second kind with argon atoms having an energy of 11.78 volts, and by electron impact. Since the percentage of electrons with velocities greater than 11.78 volts is probably small, it follows that there will be very few hydrogen molecules with an energy greater than this value. This energy is sufficient to raise the hydrogen molecule from the state N, $n=0$ to the state A, $n=a$, an interval of 11.61 volts, but not sufficient to raise it to any higher vibrational or electronic state. Returning to lower levels, all possible transitions occur, namely, A, $n'=a$ to N, $n''=0$ to 11, thereby producing the Lyman bands.

The value of a has not yet been determined. If we may assume that an appreciable percentage of the hydrogen molecules in the state A, $n=a$ have been excited by electron impact, then the states A, $n<a$ will also be excited, and instead of one series of bands there would be $(a+1)$ series. Since only one series is observed this would necessitate making $a=0$. If, however, practically all the molecules in the state A, $n=a$ have been excited by collisions of the second kind, then it is quite evident, that a may have any value in so far as the existence of a single series is concerned. The fact that argon lines of shorter wave-length than λ1048.26 occur on these plates as well as the second and third

lines of the Lyman series proves that there must be a considerable number of electrons with velocities greater than 11.78 volts. The discussion above indicates that the number of electrons per volt of velocity below 11.78 volts is considerably greater than the number per volt above 11.78 volts. One would be inclined to think, therefore, that the percentage of hydrogen molecules excited by electron impact would be appreciable, and that if a is greater than zero, at least faint series would be observed in addition to the Lyman bands. The fact such series were not observed may be considered as evidence in favor of the value $a=0$.

With this value of a the radiation potential for the Lyman bands is 11.61 volts. This is in good agreement with the experimental values[6] of a radiation potential of the hydrogen molecule, which range from 11.5 to 12.0 volts. If a were greater than zero, the value of the radiation potential would be less than 11.61 volts. The value of ω_0 for the electronic state A obtained in the latter part of this paper is 2695 cm^{-1}, which corresponds to .33 volt. From this value, it follows that if a were 1, for example, the radiation potential would be only 11.28 volts, which does not agree with the electron impact experiments as well as the former value.

It is very probable that the radiation potential of 11.61 volts is the lowest one in the hydrogen molecule. For on this theory of excitation, if any part of the secondary spectrum in the extreme ultra-violet had an excitation potential less than this value, one would expect that fact to reveal itself by the presence on these plates of one or more additional series of bands similar to the Lyman bands. Although these plates cover the entire region of the secondary spectrum in the extreme ultra-violet, no other bands were observed. Since the excitation potentials of the visible secondary spectrum[7] range from 13 to 15 volts, it is fairly certain that 11.61 volts is in fact lowest radiation potential. This conclusion is in agreement with the results obtained from electron impact experiments.[6]

Eq. (4) may now be rewritten in terms of the vibrational quantum numbers,

$$\nu=94\,075-(4267n''-113.5n''^2+\cdots). \tag{5}$$

The value of ω_0, the frequency of infinitesimal vibration for the normal state, obtained from this equation is 4267 cm^{-1} in fair agreement with the value 4880 cm^{-1} obtained by Kemble and Van Vleck[8] from specific heat data.

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[6] Bulletin of the National Research Council on Critical Potentials, pp. 114–120.

[7] O. S. Duffendack, Astrophys. J. **60**, 122 (1924).

[8] E. C. Kemble and J. H. Van Vleck, Phys. Rev. **21**, 653 (1923).

Heat of Dissociation

From Eq. (5) it follows that the vibrational energy, E_n, of the hydrogen molecule in the normal electronic state is

$$E_n = h(4267n - 113.5n^2 + \cdots). \tag{6}$$

The frequency of vibration, ω_n, of the nuclei in the vibrational state of quantum number n is

$$\omega_n = \frac{1}{h}\frac{dE_n}{dn} = 4267 - 227.n + \cdots \tag{7}$$

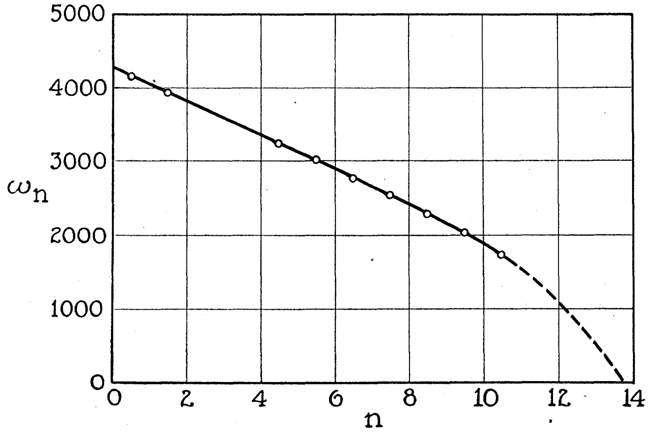

Fig. 5. The frequency of vibration of the nuclei, ω_n, in the normal electronic state of the hydrogen molecule plotted as a function of the vibrational quantum number, n.

Since the higher powers in Eq. (6) are small, dE_n/dn is practically equal to ΔE_n, if the latter be defined as

$$\Delta E_n(n+\tfrac{1}{2}) = E_n(n+1) - E_n(n). \tag{8}$$

The advantage of using the first difference is that its value may be taken directly from the experimental data, as Eq. (8) shows. Fig. 5 is a graph of ω_n or $1/h\,\Delta E_n$ as a function of n. The dotted portion of the curve is an extrapolation. The general nature of this extrapolation is justified both by the trend of the observed part of the curve and by the fact that the hydrogen molecule is homopolar. For the potential energy function of a homopolar molecule, when expressed in descending powers of the internuclear distance r, begins with a power of r equal to or greater than two, and Kratzer[9] has shown that in such cases ω_n becomes zero for a finite value of n.

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[9] A.Kratzer, Zeits. f. Physik. **26,** 40 (1924).

According to band spectrum theory the heat of dissociation of a diatomic molecule is $(E_n)_{\max}$, the maximum possible vibrational energy in the normal electronic state. As Eq. (7) shows, E_n is a maximum for that value of n at which the frequency of vibration of the nuclei is zero. It follows by integration of Eq. (7) that[10]

$$(E_n)_{\max} = h\int_0^{no} \omega_n dn \tag{9}$$

where n_0 is the value of n at which $\omega_n = 0$. Stated graphically Eq. (9) means that the area under the curve in Fig. 5 is a measure of $(E_n)_{\max}$.

Since the extrapolation in Fig. 5 is more or less uncertain it is best in estimating the value of $(E_n)_{\max}$ to get lower and upper limits as well as the probable value. The lower limit was taken as the highest observed value of the combined vibrational and rotational energies, which was obtained by subtracting the energy of the line of longest wave-length in the Lyman bands from that of the shortest wave-length. Its value is 4.10 volts or 94,600 calories per mol. The upper limit was obtained by using as an extrapolation in Fig. 5 a straight line tangent to the curve at the last observed point. Its value is 4.56 volts or 105,200 calories per mol. The probable value corresponds to the extrapolation indicated in Fig. 5. A better way of obtaining the probable value, however, is from an (n, E_n) graph. Its value is 4.34 volts or 100,100 calories per mol. These results are in accord with the best experimental values. Isnardi's result[11] (as corrected by Wohl) is that the heat of dissociation of hydrogen lies between 96,765 and 102,257 calories; while Langmuir's[12] latest value is 97,000 calories.

CRITICAL POTENTIALS

Just as the visible secondary spectrum occurs in the same general region as the Balmer series of atomic hydrogen, so the ultra-violet band spectrum of hydrogen falls in the same general region as the Lyman series. In each case there is a gap[2] between the ultra-violet and visible spectra. According to Franck[13] the visible band spectrum probably holds the same relationship to the ultra-violet band spectrum that the Balmer series does to the Lyman series. The fact that the critical potentials of the visible band spectrum[7] range from 13 to 15 volts makes this con-

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[10] Cf. R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

[11] T. Isnardi, Zeit. f. Elektrochemie **21**, 405 (1915). K. Wohl (*Ibid.*, **30**, 49, 1924) corrected a slight error in computation in Isnardi's work, thereby raising his value about 5000 calories.

[12] I. Langmuir, G. E. Rev. **29**, 153 (1926).

[13] A. Sommerfeld, Atombau and Spektrallinien, pp. 519–520.

clusion fairly certain. Furthermore, even in the visible there is a close parallel parallelism between the Balmer series and the secondary spectrum. This is shown by the diagram due to Glitscher[14] in the fourth and earlier editions of Sommerfeld's Atombau und Spektrallinien. This diagram is a photometric curve of the secondary spectrum, giving the intensity as a function of the wave number, the resolution being insufficient to show individual lines. Glitscher points out that some of the most prominent peaks on this curve have almost the same spacing as the α, β, γ, δ lines of the Balmer series. All these facts seem to indicate that there is a correlation between the electronic energy levels of the hydrogen atom and those of the molecule, and that the spacing of these energy levels is about the same in the two cases. The radiating electron in the molecule, however, is more tightly bound than the electron in the corresponding orbit in the atom. This is shown by the fact that the corresponding potentials of the molecule are always higher. Thus the ionization potential of the molecule is higher than that of the atom, and the lowest resonance potential of the molecule is 11.61 volts, whereas that of the atom is 10.15 volts. Furthermore, on the Glitscher diagram the peaks α, β, γ, δ are all on the high frequency side of the corresponding lines of the Balmer series.

These facts seem to justify an attempt to introduce total electronic quantum numbers, e_t, in the sense in which that nomenclature is used in atomic spectra. To the normal electronic level N will be assigned the value $e_t=1$, and to the electronic level A the value $e_t=2$, the difference between these two levels being 11.61 volts. On this theory the ultraviolet band spectrum is due to the transitions $e_t' \geqq 2$ to $e_t''=1$, and the visible band spectrum to the transitions $e_t' \geqq 3$ to $e_t''=2$. For the present it will be assumed that there is only one electronic energy level for each value of e_t, although the reverse is almost certainly the case in reality.

On the basis of this theory an attempt will be made to compute the higher critical potentials of the hydrogen molecule by two methods, first by use of the Glitscher diagram, secondly by use of a Rydberg formula. In the first method the assumption will be made that the peaks marked α, β, γ, δ on the Glitscher diagram represent corresponding positions in the band systems due to the transitions $e_t'=3, 4, 5, 6$ respectively to $e_t''=2$. The further assumption will be made that each peak α, β, γ, δ represents the location of the (0, 0) band for the electronic transition in question. On these assumptions by adding the voltage corresponding to each of these peaks to 11.61 volts one should obtain

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[14] K. Glitscher, Sitzungsber. d. bayer. Akad. p. 125 (1916).

the higher critical potentials and by extrapolation the ionization potential of the hydrogen molecule. This is done in Tables II and III. The values of ν are taken from the Glitscher diagram. The results of this computation are given in the second column of Table III.

In the second method the assumption is made that the critical potentials of the hydrogen molecule follow a Rydberg formula

$$V=13.539\left\{\frac{1}{(1-\alpha)^2}-\frac{1}{(e_t-\alpha)^2}\right\}. \tag{10}$$

This was suggested by the preceding theory, as well as by previous work of Fowler,[15] and Sponer.[16] The value of α was found from the lowest radiation potential by solving the equation

$$11.610=13.539\left\{\frac{1}{(1-\alpha)^2}-\frac{1}{(2-\alpha)^2}\right\}. \tag{11}$$

TABLE II

Peak	ν	$V=1.2344\times10^{-4}\nu$
α	16,650. cm^{-1}	2.055 volts
β	21,850.	2.697
γ	24,500.	3.030
δ	25,900.	3.197

TABLE III

e_t	V	V (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
∞	15.19	15.193

which gives $\alpha=0.0560$. This value of α was used in Eq. (10) to compute the series of values under V(calc). It will be observed that the agreement between the values obtained by these two independent methods is quite remarkable.

Thus far it has been assumed that to each value of e_t there corresponds only one electronic energy level of the hydrogen molecule. In reality, however, it will probably be found necessary to introduce the azimuthal and inner quantum[17] numbers also in order to classify these energy levels, so that there will be several levels for each value of e_t. Possibly the various levels corresponding to any given value of e_t are close together. That would account for the results given in Table III. In any case a consideration of the remaining electronic quantum numbers will necessitate a reinterpretation of the results in Table III and may possibly alter the numerical values. These considerations may explain the discrepancy between the value of the ionization potential, 15.19 volts,

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[15] A. Fowler, Proc. Roy. Soc. **A91,** 208 (1915).

[16] H. Sponer, Zeits. f. Physik. **34,** 622 (1925).

[17] R. T. Birge, Nature, Feb. 1926. R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 144(1926).

obtained above and the experimental values,[6] which range from 15.6 to 16.7 volts.

On the other hand this discrepancy does not necessarily indicate that one or the other of these values is wrong. For the spectroscopic values of critical potentials represent a difference of electronic energy levels, but the significance of the values obtained from electron impact experiments in the case of molecules is not yet clear. According to recent work of Franck,[18] and also Birge and Sponer,[19] if an electronic transition causes a large change in the moment of inertia of a molecule, then the transition in question, considered as a statistical average at least, cannot occur without exciting a certain minimum of vibrational energy. Where the excitation is by electron impact this additional energy of vibration must come from the impacting electron. Consequently in such cases the observed critical potentials should be higher than the corresponding difference in electronic energy levels.

This type of explanation would probably account for the discrepancy in the case of hydrogen. For, as Eq. (2) shows, there is an extremely large increase in the moment of inertia of the molecule in going from the normal level N to the excited level A. It is reasonable to suppose, therefore, that large changes in the moment of inertia occur when the molecule jumps from the normal electronic level to various higher levels or when ionization occurs. If this is the case, one would expect the observed critical potentials to be higher than the spectroscopic values.

REMARKS

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 normal molecule, D' the heat of dissociation of the ionized molecule, it follows from the principle of the conservation of energy that[20]

$$D+I_a=D'+I_m. \tag{12}$$

For hydrogen

$$I_a+D=13.54+4.34=17.88 \text{ volts}$$

If we take $I_m=15.19$ volts

$$D'=2.69 \text{ volts}$$

If we accept the experimental values of I_m, D' will be about 2 volts. Urey's[21] theoretical value is 3.12 volts. Sommerfeld,[22] on the other hand,

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[18] J. Franck, Trans. Faraday Soc. **21**, part 3 (1925).

[19] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

[20] Cf. R. T. Birge, Phys. Rev. **27**, 641 (A) (1926).

[21] H. C. Urey, Phys. Rev. **27**, 216 (1926).

[22] A. Sommerfeld, Atombau and Spektrallinien, p. 518.

assumes that $D=I_m-I_a$, which automatically makes $D'=0$. The data from positive ray analysis[23] show 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.

It is interesting to note that the First (or Red) Fulcher Band falls under the α peak in the Glitscher diagram. According to Dieke's[24] interpretation each of the so-called Fulcher Bands is a sequence of Q branches. (By a sequence is meant a group of bands for which $\Delta n = n'-n''$ is a constant.) On this interpretation the first line of the band towards the violet[25] in the First Fulcher Band is 16,611 cm^{-1}, whereas the α peak in the Glitscher diagram is 16,650 cm^{-1}. Since the α peak was assumed to represent the location of the (0, 0) band for the electronic jump $e_t'=3$ to $e_t''=2$, this fact suggests that the First Band may be an (n, n) sequence with the (0, 0) band on the violet side. Both the individual bands and the sequence as a whole are then degraded toward the red. If in addition the assumption be made that the Second (or Green) Fulcher Band is an $(n, n-1)$ sequence due to the same electronic jump, the data permit the computation of the value of ω_0 and $x\omega_0$ for the two electronic levels in question. The values obtained are:

For the state $e_t=2$,

$$\omega_0 = 2589\ \text{cm}^{-1}$$
$$x\omega_0 = 67.8\ \text{cm}^{-1};$$

For the state $e_t=3$,

$$\omega_0 = 2303\ \text{cm}^{-1}$$
$$x\omega_0 = 62.6\ \text{cm}^{-1}.$$

These values are certainly of the right order of magnitude. As evidence of that fact it will be shown that the values of ω_0 and $x\omega_0$ for the state $e_t=2$ give about the correct value for the heat of dissociation, D'', of the hydrogen molecule when in the excited state $e_t=2$. It will be assumed, of course, that in this case the molecule dissociates into one normal atom and one atom in the first excited state, $n=2$. An accurate value of D'' may be obtained from the equation

$$R_a + D = R_m + D'', \tag{13}$$

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[23] H. D. Smyth, Phys. Rev. **25**, 452 (1925); T. R. Hogness and E. G. Lunn, *Ibid.* **26**, 44 (1925).

[24] G. H. Dieke, Proc. Roy. Acad. Amsterdam **27**, 490 (1924); Phil. Mag. **50**, 173 (1925).

[25] For a table of these bands see W. E. Curtis, Proc. Roy. Soc. **A107**, 570 (1925).

which is analogous to Eq. (12). Here R_a is the lowest resonance potential of the atom, and R_m that of the molecule. Inserting the values of the known quantities

$$D''=10.15-11.61+4.34$$
$$=2.88 \text{ volts}$$

If for the electronic state $e_t=2$, the vibrational energy is

$$E_n=h(2589n-67.8n^2), \tag{14}$$

the maximum value of E_n is 3.05 volts. This is a little higher than the preceding value—a result one would expect, considering the fact that the higher powers in Eq. (14) were omitted. One should remember also that the first value applies to the upper electronic state A of the Lyman bands, and the second to the lower state of Fulcher Bands, and that these two states may not be the same.

OTHER BANDS

From Lyman's plates of the complete secondary spectrum in the extreme ultra-violet it was found that by mere inspection one could pick out groups of lines that resembled the Lyman bands. Measurements were therefore made of the lines in these groups and the usual numerical and graphical tests for bands applied. In this way some bands were found whose genuineness seemed fairly certain. Numerical relationships were found between eight of these bands and the Lyman bands, which showed that these eight bands certainly had the same final electronic state as the Lyman bands, and most probably the same initial electronic state. These relationships made possible the assignment of the vibrational quantum numbers. These bands are given in Table IV.

The value of the vibrational energy function for the electronic state A obtained from these bands is

$$E_n=h(2695n-77n^2+\cdots). \tag{15}$$

The values of the constants here are almost the same as the values in Eq. (14) for the final state of the Fulcher Bands.

The correctness of the assignment of the values of the quantum numbers may be tested by the combination relation

$$\begin{aligned} &Q(n_1',n_1'',m)-Q(n_1',n_2'',m)= \\ &Q(n_2',n_1'',m)-Q(n_2',n_2'',m)= \\ &F(n_2'',m)-F(n_1'',m), \end{aligned} \tag{16}$$

where F is the term function for the final electronic state. The differences

TABLE IV

Additional bands of hydrogen.

m	Intensity	λ	ν	Differences	
				1st	2nd
Band A ($n'=2$, $n''=1$)					
1	8	1052.63	95 000		
				127	
3	8	1054.04	94 873		
				104	
4	7	1055.20	94 769		41
				147	
5	8	1056.84	94 622		37
				184	
6	9	1058.90	94 438		
Band B ($n'=2$, $n''=2$)					
1	6	1098.01	91 074		
				113	
3	6	1099.37	90 961		
				97	
4	5	1100.54	90 864		31
				128	
5	6	1102.10	90 736		66
				194	
6	6	1104.46	90 542		26
				220	
7	6	1107.15	90 322		48
				268	
8	4	1110.45	90 054		
Band C ($n'=2$, $n''=3$)					
1	8	1144.34	87 387		
				122	
3	8	1145.93	87 265		
				76	
4	5	1146.94	87 189		48
				124	
5	7	1148.57	87 065		48
				172	
6	7	1150.84	86 893		
Band D ($n'=3$, $n''=3$)					
1	7	1115.06	89 681		
				103	
3	7	†1116.34	89 578		
				88	
4	3	1117.44	89 490		39
				127	
5	8	1119.03	89 363		45
				172	
6	7	1121.19	89 191		38
				210	
7	5	†1123.84	88 981		57
				267	
8	3	1127.22	88 714		

m	Intensity	λ	ν	Differences	
				1st	2nd
Band E ($n'=3$, $n''=4$)					
1	10	1159.76	86 225		
				115	
3	9	1161.31	86 110		
				75	
4	5	1162.32	86 035		33
				108	
5	9	1163.78	85 927		61
				169	
6	8	1166.07	85 758		
Band F ($n'=3$, $n''=5$)					
1	6	1205.07	82 983		
				107	
3	6	1206.62	82 876		
				64	
4	3	1207.55	82 812		32
				96	
5	4	1208.95	82 716		
Band G ($n'=4$, $n''=2$)					
1	4	1046.60	95 547		
				114	
3	5	1047.86	95 433		
				103	
4	3	1048.99	95 330		51
				154	
5	4	1050.68	95 176		12
				166	
6	4	*1052.52	95 010		
Band H ($n'=4$, $n''=5$)					
1	8	1174.32	85 156		
				108	
3	8	1175.80	85 048		
				63	
4	4	1176.68	84 985		47
				110	
5	8	1178.21	84 875		55
				165	
6	7	†1180.50	84 710		
Band I					
1	4	953.53	104 873		
				120	
3	5	954.63	104 753		
				106	
4	4	955.59	104 647		30
				136	
5	4	956.84	104 511		37
				173	
6	2	958.42	104 338		

†Apparently coincides with a line of the Lyman bands.
*Apparently coincides with a line of Band A.

obtained from these bands and the Lyman bands are given in Table V.

While some of the individual lines in the bands in Table IV may be incorrect, the process by which they were picked out as well as the numerical relationships would seem to indicate that on the whole they are genuine.

TABLE V

m	Band 1–Band 2	Band A–Band B	m	Band 4–Band 5	Band E–Band F
1	3929	3926	1	3244	3242
2	3921	—	2	3235	—
3	3918	3912	3	3237	3234
4	3905	3905	4	3226	3223
5	3890	3886	5	3209	3211
6	3863	3896			
m	Band 2–Band 3	Band B–Band C	m	Band 2–Band 5	Band G–Band H
1	(3690)	3687	1	10405	10 391
2	(3697)	—	2	10382	—
3	3693	3696	3	10380	10 385
4	3673	3675	4	10353	10 345
5	3661	3671	5	10303	10 301
6	3639	3649	6	10241	10 300
m	Band 3–Band 4	Band D–Band E			
1	3471	3456			
2	3450	—			
3	3450	3468			
4	3454	3455			
5	3433	3436			
6	3415	3433			

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

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HARVARD UNIVERSITY,
August 18, 1926.

Note added in proof. While the spectroscopic data given in this paper are insufficient to determine a (the value of n' for the upper electronic state A of the Lyman Bands), a consideration of the process of excitation and the experimental values of the lowest radiation potential of H_2 led us to the probably conclusion that $a=0$. G. H. Dieke and J. J. Hopfield have recently shown, however, (private communication) from their admirable analysis of the absorption spectrum of the hydrogen molecule that this conclusion is incorrect and that $a=3$. This, of course, alters the value of the lowest radiation potential. Their value is 11.1 volts. They also find a third electronic level at 12.2 volts above the normal level N. Designating this level as B, the *other bands* in this paper are due, according to their analysis, to the electronic transition $B \rightarrow N$. It might seem that these changes would entirely invalidate the results given in Table III. Such is not the case, however. For, using the terminology above, it seems probable that both the electronic level A at 11.1 volts and B at 12.2 volts have the value $e_t = 2$. The upper of these two orbits is evidently more hydrogen-like, and is therefore the better one to use in computing the probable values of the higher critical potentials. Using 12.2 everywhere instead of 11.61 volts in computing the values of V and V (calc) in Table III, one obtains the results given in Table IIIa.

TABLE IIIa

e_t:	2	3	4	5	6	∞
V:	12.20	14.26	14.90	15.23	15.40	15.78
V (calc):	12.20	14.275	14.98	15.30	15.47	15.86

The value of α used in computing V (calc) from Eq. (10) was $\alpha = 0.0760$. The agreement between V and V (calc), though not as good as in Table III, is still fair, and, what is perhaps more significant, the resulting value of the ionization potential is in good agreement with the best experimental values. In accordance with our previous statements the values in Table IIIa should not be regarded, strictly speaking, as the only higher critical potentials of H_2, but rather as one of several Rydberg or Ritz series.

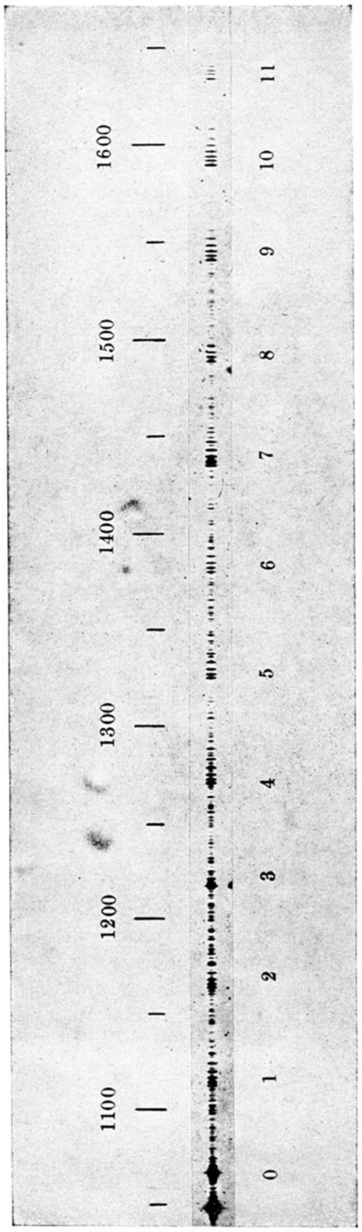

Fig. 1. The Lyman Bands.