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THE QUANTUM LEVELS AND RESULTING CONSTANTS OF THE HYDROGEN MOLECULE

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Richardson[1] seems to have obtained the much-sought-for connection between the visible and ultra-violet bands of hydrogen. The resulting value of the ionization potential, as recalculated by the writer from Richardson's data, is 15.34 volts. Richardson seems to think that such a low value cannot be reconciled with the observed value of about 16 volts. A similar discrepancy occurs several times in Richardson's earlier work.

It appears to the writer quite certain that the discrepancy is only apparent. Burrau[2] has calculated the total energy of H_2^+, on the basis of the new wave mechanics, as $1.204\,R$, or $16.30\,(\pm 0.03)$ volts, since $R = I_A = 13.54$ volts, the ionization potential of the hydrogen atom.[3] This total energy of H_2^+ is the ionization potential of the ion, which we shall denote by I'_M. Assuming Witmer's spectroscopic value for the heat of dissociation of the neutral molecule, $D = 4.34$ volts, we have for the ionization potential of the neutral hydrogen molecule, $I_M = D + 2I_A - I'_M = 15.12$ volts, as compared to the above value of 15.34 volts. Furthermore, Condon,[4] using Burrau's result and making certain reasonable assumptions, has calculated the total energy of H_2 as approximately $2.325\,R$, or 31.48 volts. This gives $D = 4.40$ volts, and $I_M = 15.18$ volts $(31.48 - 16.30)$. In addition, Condon shows that the most probable transition from the normal, non-vibrating state of H_2 to the normal state of H_2^+ produces 1.07 volts of vibrational energy, giving an *apparent* mean ionization potential of 16.25 volts, as measured by electron impact methods. This indirect acquisition of vibrational energy accompanying an electronic transition is now well established, although Condon's numerical value may, of course, be slightly in error.

Some of Richardson's results are given in terms of the new wave me-

chanics, others in terms of the old quantum mechanics. In much of his work on heats of dissociation a value of 15.9 volts has been assumed for I_M, as well as Langmuir's value of 4.21 volts for the heat of dissociation of hydrogen. For these reasons the writer has felt it profitable to work through much of Richardson's data, reducing all the results to a standard basis. The *old* mechanics have been adopted, since this leads to values of the energy levels connected more closely with the observed frequencies. Each electronic level, as given in table 1, thus refers to the molecule with a half unit of vibrational energy, on the interpretation of the new mechanics. Each electronic level of the new mechanics lies beneath that of the old mechanics by the amount

$$s = \omega^0/2 \; + \; \omega^0 x/4.$$

The vibration frequency of the new mechanics ($\bar{\omega}^0$) equals $\omega^0 + \omega^0 x$.

TABLE 1

LEVEL	E_e (CM.$^{-1}$)	DEN.	ω^0 (CM.$^{-1}$)	$\omega^0 x$ (CM.$^{-1}$)	I_0 $\times 10^{40}$	r_0 $\times 10^8$	$I_0\omega^0$
$1^1S(A)$	zero	0.9396	4262	113.5	0.480	0.76	20500
$2^1S(B)$	90083	1.7920	1325	15.9	1.99	1.55	26400
2^3P	(94735)	(1.9281)	2390	73	0.78	0.97	18700
2^3S	94906.7	1.9337	2593.82	68.41	0.965	1.08	25000
2^1P	(95469)	(1.9526)	.....	....	...	...	...
(C)	99086	2.0882	2380	66.5	0.942	1.06	22400
3^3S	111427	2.9261	.....	....	...	...	...
3^3P	111518.1	2.9365	2306.94	62.94	1.072	1.136	24700
3^1P	111656.8	2.9526	2373.89	12.36(?)	...	...	...
4^3P	117169.9	3.9395	2276.45	63.08	1.089	1.145	24800
4^1P	117216.9	3.9526	2325.6(?)	....	...	...	...
5^3P	119744.2	4.941	2251	58(?)	1.135	1.168	25500
6^3P	121130.2	5.942	2229(?)	54(?)	1.130	1.166	25200
7^3P	121961.0	6.942	.....	....	...	...	...
8^3P	122498.3	7.942	.....	....	...	...	...
$H_2{}^+$	124237	∞	2247	61.4	0.927	1.056	20800

The value of $\omega^0 x$ is not changed. The nomenclature is that of the National Research Council Report on Molecular Spectra.[5]

In table 2 are listed the various band systems with the origin (ν_e) of each, from which are derived the energy levels of table 1. In general, the value of ν_e is merely the frequency of the first line of the Q branch, but the error thus introduced is negligible. Richardson's recent conclusions are based entirely on the identification of the lower level of his "A" and "B" bands with Dieke and Hopfield's "B" level (2^1S). The agreement is very striking. Thus the vibrational level intervals, as measured by Richardson are 1313.26, 1276.42 and 1247.67 cm.$^{-1}$, while the same intervals, as measured by Dieke and Hopfield,[6] from the ultra-violet absorption bands, are 1313, 1276 and 1247 cm.$^{-1}$

Richardson considers that the *upper* levels of the A and B bands are 3^1P and 4^1P, and with an assumed Rydberg formula the writer finds

$$\nu = 34{,}154 - 109{,}678.3/(m - 0.0474)^2.$$

The total uncertainty in the "head" of this series should not be greater than about 100 cm.$^{-1}$ Richardson finds a very few lines belonging possibly to bands corresponding to the transition from 5^1P to 2^1S, and uses these also, in a Ritz formula, to get the head of the series at 33,727 cm.$^{-1}$ on the new mechanics, or approximately 34,215 cm.$^{-1}$ on the old. The difference between the Rydberg and Ritz formulas is only 61 cm.$^{-1}$ and, therefore, negligible.

We thus have the term value of the 2^1S level. The normal "A" level lies 90,083 cm.$^{-1}$ below this. Hence, $90{,}083 + 34{,}154 = 124{,}237$ cm.$^{-1}$ = 15.34 volts = I_M, on the basis of the old mechanics. With this value established, the remaining values of table 1 follow immediately. Richardson's very reliable value of 29,330.3 cm.$^{-1}$ for the head of the α-β-γ series of bands has been used as the term value of the 2^3S level. The second column of this table gives the frequency of the level measured *up* from the normal

<div align="center">TABLE 2</div>

SYSTEM	TRANSITION	ν_s
A-B (Lyman) bands	1^1S-2^1S	90083
A-C (Werner) bands	1^1S-(?)	99086
"A" bands	2^1S-3^1P	21573.8
"B" bands	2^1S-4^1P	27133.9
....	2^3P-3^3S	16692.0
"α" bands (Fulcher)	2^3S-3^3P	16611.43
"β" bands	2^3S-4^3P	22263.24
"γ" bands	2^3S-5^3P	24839.05
"δ" bands	2^3S-6^3P	26224.21
"ϵ" bands	2^3S-7^3P	27054.45
"ζ" bands	2^3S-8^3P	27592.52

level, as is customary in the case of molecules, while the third column gives the "denominator" $(\sqrt{109678.3/\nu})$, where ν is the term value measured *down* from ionization, as ordinarily employed in the case of atomic spectra.

The adopted values of $I_M = 15.34$ volts and $D = 4.34$ volts (35,154 cm.$^{-1}$) can be checked indirectly by considering the heat of dissociation of the molecule in excited levels. This method has been tried by Richardson[7] and led to the discrepancies noted earlier in this paper. With the new values, the discrepancies disappear. Thus, one may first excite a molecule with electronic energy E_e^x and then dissociate it with vibrational energy D^x (where x is any electronic level). The products of dissociation from an excited molecular level are one normal and one excited atom, according to a considerable amount of experimental evidence which has now accumulated. Hence the total energy just given should equal the energy of dissociation into two normal atoms (D) plus the energy of excitation of one of the atoms (E_A^x), or $E_e^x + D^x = D + E_A^x$.

In order to get D^x, I have used the linear extrapolation of the ω^x: n

curve which Birge and Sponer[8] found so successful in the case of various non-polar molecules. For the 3^3P and 4^3P levels, one thus obtains $D^* = 21,120$ and $20,520$ cm.$^{-1}$, respectively. The dissociation products from these two levels include presumably one hydrogen atom excited to the $3P$ and $4P$ level, respectively. With the known values of E_A^* (97,491 and 102,823 cm.$^{-1}$) one obtains, by this indirect process, $D^* = 21,127$ and $20,807$ cm.$^{-1}$, respectively, in perfect agreement with the above directly calculated values. A similar calculation for the 2^3S level gives $D^* = 24,580$ cm.$^{-1}$ by the direct, and $22,505$ cm.$^{-1}$ by the indirect method. This discrepancy of 0.26 volt is more nearly that to be expected, and would vanish for $I_M = 15.08$ volts. The $\omega^n : n$ curves for the ^1P levels are not well enough known for extrapolation. The curve for the 2^1S level has been linearly extrapolated by Dieke and Hopfield with a resulting value of $D^* = 3.1$ volts. I have, however, recalculated the values of ω^0 and $\omega^0 x$, from their data, and have obtained those given in table 1, in place of their values of 1336.7 and 18.42. The new values give 3.41 volts for D^* while the indirect calculation gives 3.37 volts.

For the "C" level we have the recent very reliable data of Hori,[9] which give 99,086 for E_e, and a number of determinations for most of the vibrational level intervals. These are very consistent among themselves but the resulting average values, 2314, 2168, 2050, 1903 and 1783 cm.$^{-1}$ show the curiously oscillating differences 146, 118, 147 and 120 cm.$^{-1}$. The *average* value of $2\omega^0 x$ is thus 133 cm.$^{-1}$, but obviously this is very untrustworthy. The resulting value of ω^0 is 2380, as given in table 1. This gives $D^* = 2.64$ volts, as compared to an indirect measurement of 2.27 volts. Of course, the direct and indirect values of D^*, for the B and C levels, do not throw any light on the value of I_M. They merely test the accuracy of a linear extrapolation of the ω^n curve, and in the case of the B level, where the ω^n values lie on a fairly smooth curve, the agreement is satisfactory.

The numerical values for the respective separations of the vibrational levels of the normal state (1^1S), as measured by Witmer,[10] Dieke and Hopfield[6] and Hori,[9] are essentially the same. The values of ω^0 and $\omega^0 x$, as published by these various investigators, are, however, in poor agreement. I have accordingly used the data of all three investigators to obtain the constants given in table 1, which agree most nearly with those given by Witmer. In this connection it should be noted that the separations of the first few vibrational levels lie on a very smooth curve, with the exception of the $n = 0$ to 1 interval. The best observed value is 4159 cm.$^{-1}$ while the calculated value is 4148 cm.$^{-1}$ This apparent *vibrational perturbation* is similar to that noted by the writer,[11] in the case of the final state of the Ångstrom bands of CO. With the accurate data now becoming available, evidences of such vibrational perturbations are begin-

ning to accumulate and should prove of some theoretical importance.

The values of ω^0 and ω^0x for H_2^+, in table 1, are obtained as follows: Knowing the values of ω^0 and ω^0x for any electronic level, one can obtain s, the shift in this level, on passing to the new mechanics. The corresponding new value of the origin of any band system $(\bar{\nu}_e)$ is then given by $\bar{\nu}_e = \nu_e + s'' - s'$. One thus obtains, for the A and B levels, $\bar{\nu}_e = 21,056.7$ and $26,647.1$ cm.$^{-1}$ Using these values in a Rydberg formula, one finds $33,688$ as the new term value $(\bar{E}_e)$ of the 2^1S level, compared to Richardson's value of $33,727$ cm.$^{-1}$, obtained with a Ritz formula as previously noted. Denoting by s^+ the value of s for the normal level of H_2^+, we have $s^+ = E_e + s - \bar{E}_e$, where E_e, s and $\bar{E}_e$ refer to any one electronic level of H_2. We thus obtain, using the 3^1P and 4^1P levels, $s^+ = 1139$ cm.$^{-1}$ Such a process is essentially equivalent to extrapolating the values of s for a set of levels of H_2 differing only in the value of the total quantum number n to $n = \infty$. In other words, if an electron is removed, step by step, from a molecule, the constants of the molecule should change gradually into those of the molecule ion. This value of $s^+ = 1139$ cm.$^{-1} = 0.141$ volt is in good agreement with Burrau's theoretical value [20] of 0.14 volt. We know also the heat of dissociation for the normal level of H_2^+. It is $D' = 4.34 + 13.54 - 15.34 = 2.54$ volts, or $20,570$ cm.$^{-1}$ If one assumes a linear curve for ω'', then $D' = \omega^{0^2}/4\omega^0x$. Hence, knowing s^+ and D' we obtain ω^0 and ω^0x for this level, as listed in table 1.

In an earlier article, Richardson[12] discussed the band system 2^3P-3^3S of table 2, and concluded that the final state of this system (2^3P) was identical with the "C" level of Dieke and Hopfield. This identification yields $I_M = 15.84$ volts, on the old mechanics, in good agreement with the value expected by Richardson. The identification is based on values of ω^0 and ω^0x for the 2^3P level, of approximately 2390 and 73, as given in table 1. These are to be compared with the corresponding values of 2380 and 66.5, obtained from Hori's new data. Richardson used the older data by Werner[13] for the A–C bands, and a somewhat different interpretation, and obtained a much better check. It is evident from table 1, however, that we cannot simultaneously assume the identification of the C and 2^3P levels, and the B and 2^1S levels. In order to do this, Richardson, in the last part of his recent article,[1] suggests an entire rearrangement of the "B" band system. The writer can see no justification for this rearrangement or for the assumption that the levels C and 2^3P are identical.

The C level is thus left with no theoretical designation. This, however, is no longer a serious objection. Both Richardson[7] and the writer[14] have suggested that the molecule H_2 should be similar to the atom He and should, therefore, have triplet and singlet series. The C level, from its general characteristics, is a ^3P level. It is not the 2^3P level, as we have seen. Still less can it be the 3^3P level. Now Hund,[15] in an extremely

important series of papers, in which the new wave mechanics are applied in some detail to molecular structure, has shown that there are more molecular levels of H_2 than there are atomic levels of He.   The C level is, therefore, doubtless one of these extra levels, dissociating into the $n = 2$ state of the hydrogen atom, just as do the known 2^1S, 2^3P and 2^3S levels of H_2.

In all of Richardson's work, and in the discussion given thus far in the present paper, the connection between the ultra-violet and the visible bands of H_2 has been based solely on the spacing of the vibrational energy levels.   If the identity of certain levels is correct, there should be corresponding identities for the spacing of the rotational energy levels, as shown by the value of the moment of inertia (I_0).   Unfortunately, it has not been possible thus far to obtain trustworthy values of I_0 for the various levels of H_2.   The only exception to this statement may be in the case of Hori's recent work.   He has obtained new measurements for the A-C (Werner) bands, showing quite surely P, Q and R branches in each band.   As usual the "crossing-over" of the Q branch makes it impossible to test the combination principle by means of the Q-P and R-Q relations, but it *is* possible to test it with the R-P relation.[16]   Hori thus gets satisfactory values for the spacing of the rotational levels for the normal electronic level, and a value $I_0 = 0.480 \times 10^{-40}$ gm. cm.^{2}, in terms of the *old* mechanics.   His published value (0.467) is in terms of the new mechanics, which, as already noted, interprets the former value as referring to a molecule with a half unit of vibrational energy.   Since I_n always increases with n, the new mechanics value $\bar{I}_0$ will always be less than the old mechanics value I_0. More explicitly, $\bar{B}_0 = B_0 + \alpha/2$ where $B_n = B_0 - \alpha n$ and $\bar{I}_0 = 27.70 \times 10^{-40}/\bar{B}_0$.   Hori obtains $I_0 = 0.942 \times 10^{-40}$ for the C level.

For the A-B (Lyman) bands, the analysis is much less complete.   Hori re-analyzes Witmer's published data[10] for the A_n-B_3 progression, obtaining a short R branch and another longer and stronger branch.   This latter may be a P, a Q or a combined P and Q branch.   Assuming it to be a P branch, he obtains values of ΔF for the A level, agreeing well with those obtained from the Werner bands.   The possible test equalities are, however, very few in number.   With this interpretation he obtains $B_3 = 12.103$ cm.$^{-1}$ for the B level.   This value is at least roughly correct, as may be seen from the following.   In the case of a P, Q or R branch, the second difference of the successive lines equals $2C$, where $2C = 2(B' - B'')$. The Werner and Lyman bands are known, from the absorption work of Dieke and Hopfield, to have the same lower level.   Hence the value of B'' for the Lyman bands necessarily equals that for the Werner bands. Thus, *regardless* of the interpretation of the observed branches in the Lyman bands, we obtain a value of $2C$, giving in turn a value of B_3 for the upper level of the Lyman bands.   The data show that this value (for the $n = 3$ level) is certainly close to 12.1 cm.$^{-1}$

One can obtain an approximate value of B_0 for the $n = 0$ level as follows: For the A level, $\alpha = 2.7$, according to Hori's work, and $B_0 = 57.77$. Hence, $\alpha/B_0 = 0.047$. For the C level $\alpha = 1.2$ and $B_0 = 29.4$. Hence, $\alpha/B_0 = 0.041$. The near equality of these two ratios seems significant. If then we assume $\alpha/B_0 = 0.044$ for the B level, we have $B_3 = 12.10 = B_0 - 3\alpha = B_0 (1 - 0.132)$. Hence, $B_0 = 13.94$ cm.$^{-1}$ or $I_0 = 1.99 \times 10^{-40}$ gm. cm.^{2} for the B level. This is a surprisingly large value, especially as compared to the value of I_0 for H_2^+. That the relative values of I_0 for the A, B and C levels are, however, reasonable can be seen by comparing the values of $I_0\omega^0$ as given in the last column of table 1. This product has been found to be roughly constant, for the various levels of other molecules.

Richardson has not as yet been able to apply the combination principle in the case of any of the visible bands of hydrogen. He has calculated rough values of the moments of inertia by using certain theoretical relations between vibrational and rotational energy constants,[17] together with certain additional assumptions. Some of the theoretical relations just mentioned have been found true in the case of rather rigid molecules having long band series, but it seems to the writer questionable how far they can be trusted in the case of a very deformable molecule like hydrogen, especially with such fragmentary data available. Richardson's value of $2B_0$ (= his $u\omega^0$) for the 2^1S level is 55.7 and is especially uncertain. It, however, is almost exactly twice the value of $2B_0 = 27.88$, just obtained for the B level, which is certainly identical with the 2^1S level. It may be noted that Richardson's value of $2B$ is practically the same for the other excited levels, although the value of ω^0 is twice as large. In other words, the value of $I_0\omega^0$ is roughly the same for all the levels of H_2, as shown in table 1, but if Richardson's value of $2B_0$ for the B level is used, this product is only 13,200. It is, therefore, possible that in some way a factor of two has been introduced into Richardson's analysis of this level. For the 2^3P level Richardson obtains $I_0 = 0.78 \times 10^{-40}$, while for the C level Hori obtains 0.94×10^{-40}. This discrepancy would appear to rule out the suggested identity of these two states, but it must be remembered that Richardson's value is very uncertain. Richardson's values of I_0 for various other levels, together with all values of the nuclear separation r_0[18] are given in table 1.

The above analysis thus indicates that Richardson's identification of the B level of Dieke and Hopfield with the final level of his A and B bands is justified by the vibrational level intervals, and by the direct and indirect evaluation of the various heats of dissociation. It is justified by the rotational level intervals only if Richardson's value of $2B_0$ is halved, giving $I_0 = 1.99 \times 10^{-40}$ for this common level, in agreement with Hori's analysis. The identification of the 2^3P and C levels is inconsistent with

the previous identification, while the expected equalities among the rotational and vibrational energy levels are not conclusive for or against this assumption.

Assuming then the first identification, we have the relations given in tables 1 and 2 leading to $I_M = 15.34$ volts, with $D = 4.34$ volts assumed for the neutral molecule and $I'_M = 16.08$ volts $(4.34 + 2 \times 13.54 - 15.34)$, and $D' = 2.54$ volts for the ionized molecule, all in terms of the *old* mechanics. In terms of the new wave mechanics $I'_M = 16.22$ volts, as compared to Burrau's theoretical value of 16.30 volts (or to a value of 16.46 volts recently calculated in a somewhat similar way by Niessen[19]) while $I_M = 15.46$ volts. Hence, $I'_M + I_M = 31.68$ volts, as compared to Condon's approximate theoretical value of 31.48 volts. Finally, if Burrau's theoretical value of $I'_m = 16.30 \pm 0.03$ volt is assumed to be correct, then $D = 4.42$ volts, instead of 4.34 volts as assumed throughout this paper.

[1] Richardson, *Proc. Roy. Soc.*, **A115**, 528, 1927.

[2] Burrau, *Naturwiss.*, **15**, 16, 1927, and *Kong. Danske Vid. Selsk. Math.-fys.* **7**, No. 14, 1927.

[3] The most probable values of the basic constants e, c and h now are $e = 4.774 \times 10^{-10}$ es., $c = 2.99796 \times 10^{10}$ cm. sec.$^{-1}$, $h = 6.557 \times 10^{-27}$ erg sec., yielding 8100 cm.$^{-1}$ = one volt.

[4] Condon, *Proc. Nat. Acad. Sci.*, **13**, 466, 1927.

[5] Bull. Nat. Res. Coun., Vol. 11, Part 3, 1926, "Molecular Spectra in Gases." To be referred to as "Report."

[6] Dieke and Hopfield, *Z. Physik*, **40**, 299, 1926, and *Phys. Rev.*, **30**, 400, 1927.

[7] Richardson, *Proc. Roy. Soc.*, **A113**, 368, 1926 (see page 415), and *Ibid.*, **A114**, 643, 1927 (see page 649).

[8] Birge and Sponer, *Phys. Rev.*, **28**, 259, 1926.

[9] Hori, *Z. Physik*, **44**, 834, 1927.

[10] Witmer, *Phys. Rev.*, **28**, 1223, 1926.

[11] Birge, *Ibid.*, **28**, 1157, 1926.

[12] Richardson, *Proc. Roy. Soc.*, **A114**, 643, 1927.

[13] Werner, *Ibid.*, **A113**, 107, 1926.

[14] "Report," page 229.

[15] Hund, *Z. Physik*, **40**, 742, 1927, and **42**, 93, 1927.

[16] "Report," page 147.

[17] *Ibid.*, page 108.

[18] *Ibid.*, page 223. For H_2, $\mu = 0.8314 \times 10^{-24}$. The values of I_0 and r_0 for H_2^+ are from Burrau.[2] ($r_0 =$ two Bohr units.)

[19] Niessen, *Z. Physik*, **43**, 694, 1927.

[20] Dr. E. U. Condon has kindly called the writer's attention to the fact that on page 13 of Burrau's Danish Academy paper, the equation should read $2/M$ in place of $1/2M$. This gives $s^+ = 0.14$ volt, instead of Burrau's published value of 0.07 volt.