Letters to the Editor.

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The Hydrogen Molecule.

RECENT experimental and theoretical work by Richardson, Witmer, Dieke and Hopfield, Hori, Burrau, Condon, Dennison, Sugiura, and others, makes possible a reasonably certain determination of the more important constants of the hydrogen molecule and molecule ion. In order to compare the results of different investigators, it is essential that these be calculated consistently according to some adopted interpretation, and with definite values of the basic constants. I should like especially to emphasise the necessity of distinguishing results in terms of the new wave mechanics from those in terms of the older quantum mechanics. Failure to make such a distinction has already led to a number of errors in the published literature.

In a paper which will appear shortly in the *Proc. Nat. Acad. Sci.*, I have given the more important details concerning such a recalculation and inter-comparison of the available data for hydrogen. The purpose of the present communication is to examine critically the results and to consider certain additional facts and conclusions. All data and constants are given here in terms of the *old* mechanics. Transformation equations for the two systems are given in the paper just mentioned.

Richardson (*Proc. Roy. Soc., A*, **115**, 528; 1927) has definitely identified the final (lower) state of his 'A' and 'B' bands with the initial 'B' state of the A-B ultra-violet bands of Dieke and Hopfield. With an assumed Rydberg formula for the upper levels of these two systems, one obtains 15.34 volts for the ionisation potential of the neutral molecule. This should be accurate to about 0.01 volt. Richardson believes that this value cannot be reconciled with the electrical determination of about 16 volts, but Condon has shown that such an apparent discrepancy is to be expected, and the chief object of the present work is to show that this lower value is entirely satisfactory.

If I_M and I'_M represent the ionisation potentials of the neutral and ionised hydrogen molecule respectively, D the normal heat of dissociation, and I the ionisation potential of the atom, then $I_M + I'_M = D + 2I_A$. Of these four quantities only I_A (=13.54 volts) is accurately known. For the other three quantities we have the following data. The best value of D is 4.34 ± 0.1 volts from Witmer's extrapolation of the vibrational levels of the normal state. (Dieke and Hopfield's determination of 4.38 volts is based on a probable misinterpretation of the spectrograms, according to later unpublished work by Hopfield.) The best value of I'_M is 16.16 ± 0.03 volts, as calculated by Burrau (*Danske V. S. Math.-fys.*, **7**, No. 14; 1927). His result of $1.402 R$ (=16.30 volts) is in terms of the *new* mechanics. Dr. E. U. Condon has directed my attention to the fact that, due to an error in one of Burrau's formulae, the correcting factor (s^+) should be 0.14 volt, and not 0.07 volt as calculated by Burrau.

With $I_M = 15.34$ volts, there is just 0.08 volt discrepancy between the three suggested values. I believe it most probable that I_M and I'_M are correct, as given, and that $D = 4.42$ volts. The value of $I_M = 15.34$ volts can be checked also by means of the heats of dissociation in the various excited states of

the molecule. In the case of every level for which data are available, the agreement, as shown in my longer paper, is remarkably good.

The recent work of Hori gives 0.48×10^{-40} as a very trustworthy value of I_0 , the moment of inertia of H_2 in the normal state, and this checks with Dennison's value from the specific heat curve. For the 'B' level only B_3 is reliably known, but with a reasonable assumption as to the value of a ($B_n = B_0 - an$), I obtain B_0 and finally $I_0 = 1.99 \times 10^{-40}$. This is just twice the value given by Richardson, but is the value to be expected in view of the very small magnitude of ω_0 for this level. The process by which Richardson calculates I_0 from known vibrational data, plus the value of a , but *without* knowing B_0 , is most interesting. It is based on Kratzer's expression for the potential function of a *polar* molecule and gives for I_0 a value 5 per cent. too low, as applied to HCl.

So far as I know, Richardson's method has never been tested on a non-polar molecule. I have accordingly carried out such a test for several non-polar molecules for which trustworthy data are available and find that this method gives values of I_0 ranging from 8 per cent. too large for the excited level of the Swan bands to 9 per cent. too small for the excited level of the CN violet bands. Assuming Hori's values of I_0 for the normal and the 'C' level of H_2 , the same method gives results 21 per cent. and 26 per cent. too large respectively. Using my own probable value of a (0.614) for the B level, the Richardson method is correct to within 3 per cent. His value of $a = 2.22$ is derived from extremely uncertain data and cannot be correct, since even with his own doubled value of B_0 (27.8), it indicates that the mean moment of inertia becomes infinite for only 12.5 quanta of vibrational energy. The vibrational data, on the other hand, show that at least 42 quanta are needed. Richardson's other values of I_0 are probably roughly correct, and the product $I_0\omega_0$ shows the expected rough constancy for *all* levels, including the B level, if $I_0 = 1.99$ is used.

By extrapolating to ionisation the values of ω_0 in a given Rydberg series, one obtains an estimate of ω_0 for the normal state of H_2^+ . My own result for this is 2247 cm^{-1} , which corresponds to $s^+ = 0.141$ volt, in remarkable agreement with Burrau's value (*as corrected*), calculated directly on the new mechanics. The heat of dissociation of H_2^+ is given by $(D + I_A - I_M)$, and with the values finally adopted equals 2.62 volts. Burrau calculates I_0 for H_2^+ as 0.927×10^{-40} , and the fact that more than *double* this value is found in the B level of H_2 is most astonishing, and has interesting consequences.

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Spatial Distribution of Photoelectrons Produced by X-rays.

JUDGING from recent papers on this subject, there seems to be considerable diversity of opinion concerning the explanation of the *dispersion* or 'spread' of the photoelectrons, whilst there appears to be no disagreement about the cause of the *longitudinal asymmetry*, which is generally assumed to correspond to the transfer to the photoelectrons of the momentum of the absorbed radiation. J. M. Nuttall, H. S. Barlow, and the present writer (hereinafter referred to as N.B.W.) recently investigated the longitudinal distribution of photoelectrons, and the results (not yet published) indicate an average forward component of momentum of the photoelectrons which is appreciably greater than the momentum, $h\nu/c$, of an incident quantum. The writer has also made a closer