

¹¹ G. Goudsmit and R. de L. Kronig, *Versl. Akad. Amsterdam*, **34**, no. 2; also R. de L. Kronig, *Zs. Physik*, **31**, 885 (1925).

¹² H. N. Russell, *Proc. Nat. Acad. Sci.*, **11**, 314 (1925), especially p. 319.

¹³ N. Bohr, *The Quantum Theory of Line Spectra, Copenhagen*, p. 85; *Zs. Physik*, **13**, 149 (1923); *Die Naturwissenschaften*, **12**, 1115 (1924).

¹⁴ W. Heisenberg, *Zs. Physik*, **31**, 617 (1925).

¹⁵ J. A. Eldridge, *Physic. Rev.*, **24**, 234 (1924).

¹⁶ Hanle also predicts an angle of 54.7° , but it is not clear whether he uses the classical or quantum view-point.

¹⁷ W. Hanle, *Zs. Physik*, **30**, 93 (1924).

¹⁸ For greater detail see Gaviola and Pringsheim,⁴ p. 372, ff., or Breit,² p. 835.

¹⁹ L. S. Ornstein, H. C. Burger and W. C. van Geel, *Zs. Physik*, **32**, 681 (1925).

²⁰ The writer is unable to agree with a statement made by Ellett⁸ that according to the quantum theory we may likely expect zero polarization in case (*d*).

²¹ Cf. Gaviola and Pringsheim,⁴ p. 372.

THE STRUCTURE OF THE HYDROGEN MOLECULE ION

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If the condition of dynamic stability is ignored, the steady state of lowest energy of the hydrogen molecule ion should be that in which the electron vibrates in a straight line perpendicular to the line joining the nuclei and through the middle point of this line. The energy of this steady state has been calculated using the following assumptions: the inverse square law of force is assumed to hold between the electron and the positive nuclei, the motion of the electron is described by classical mechanics and the steady states fixed by the Wilson-Sommerfeld quantum conditions, and finally the mean value of the component of the force of attraction between the electron and one nucleus is set equal to the force of repulsion between the two nuclei. This model is dynamically unstable with respect to a displacement of the electron in the direction of the line joining the nuclei at least when the nuclei are not rotating.

The results of the calculations can be briefly summarized and will be published in greater detail elsewhere. The phase integral has been taken over one complete oscillation of the electron, i.e., from a point farthest from the line joining the nuclei to the farthest point on the opposite side of this line and back to the original position. The energy for these steady states in which the electron is moving in a straight line perpendicular to the line joining the nuclei (hereafter referred to as the vibration orbits) is given by the relation

$$W = -\frac{Rhc_1}{n^{*2}} \frac{8(\Pi_1(n,k) - 2E(k) + K(k))^2}{\pi^2} \left(\frac{4}{B} - 1\right). \quad (1)$$

In this formula R is the Rydberg constant, h Planck's constant, c_1 the velocity of light and n^* the quantum number. B is the ratio of the distance between the electron and one nucleus, when it is farthest from the line joining the nuclei, and one-half the distance between the nuclei. $K(k)$, $E(k)$, and $\Pi_1(n,k)$ are the complete elliptic integrals of the first, second and third kinds, respectively, having the modulus $k = 1/2(1 - 1/B)$ and the parameter $n = (1 - 1/B)$. B and therefore $K(k)$, $E(k)$ and $\Pi_1(n,k)$ are further subject to the condition that

$$\frac{B}{8} \Pi_1(n,k) - \left(1 - \frac{B}{8}\right) (2E(k) - K(k)) = 0, \quad (2)$$

this being the final form of the condition that the mean force acting on the nuclei in the direction of the line joining them shall be zero. The distance between the nuclei is given by the relation

$$\frac{2c}{a} = \frac{\pi^2 n^{*2}}{4(\Pi_1(n,k) - 2E(k) + K(k))^2}, \quad (3)$$

a being the radius of the first Bohr orbit of the hydrogen atom and c half the distance between the nuclei. Equation (2) has been solved by trial and the values of B , $K(k)$, $E(k)$ and $\Pi_1(n,k)$ so secured have been substituted in equations (1) and (3). With the numerical values substituted these two equations become, respectively,

$$W = -Rhc_1 \frac{1}{n^{*2}} 1.2300, \quad (4)$$

$$\frac{2c}{a} = 1.051 n^{*2}. \quad (5)$$

The ionizing potential calculated is 16.65 volts. This agrees well with that observed by Olson and Glockler.¹ Eight of the nine potentials observed by these authors can be represented by the formulae

$$V = 3.15 + 13.53 \left(1 - \frac{1}{n^2}\right), \quad n = 3, 4, 5, 6, 7 \text{ and } \infty \quad (6)$$

and

$$V = 16.68 \left(1 - \frac{1}{n^2}\right), \quad n = 3, 4 \text{ and } \infty. \quad (7)$$

The latter formula was called to the writer's attention by Dr. A. R. Olson at the time their work was published in 1923. The theoretical formula

from the value of the ionizing potential for the model suggested here for dissociation of the hydrogen molecule ion and resonance of the atom to higher quantum states is

$$V = 3.12 + 13.53 \left(1 - \frac{1}{n^2}\right), n = 2, 3, 4, \dots, \quad (8)$$

and for resonance of the $H\frac{1}{2}^+$ ion to higher steady states

$$V = 16.65 \left(1 - \frac{1}{n^{*2}}\right), n^* = 2, 3, 4, \dots, \quad (9)$$

The close agreement between the potentials observed by these two men and those calculated here is quite remarkable. A study of the conditions of the Olson and Glockler experiment shows that it is possible to interpret their data in accordance with the theory, i.e., as being due to the hydrogen molecule ion and not to the molecule. If the electrometer current which they measured is due to ions only, and if the ionizing potential of the hydrogen molecule lies above 13.27 volts and below 14.80 volts, which are the critical potentials calculated from formula (4) for n^* equal to 2 and 3, respectively, the absence of the experimental value for n equal to 2 in formula (6) is explained. No current would be observed until $H\frac{1}{2}^+$ ions are produced and if these are first produced above the 13.27 volt point, this point could not be observed. This gives a possible explanation of this unexpected and puzzling point in their work.

If then we adopt 14.84 volts (Olson and Glockler's lowest potential) as a maximum for the ionizing potential of the molecule, and 16.65 volts as that of the hydrogen molecule ion, a maximum value for the heat of dissociation of the molecule can be calculated by adding these two numbers and subtracting twice the ionizing potential of the hydrogen atom,

$$14.84 + 16.65 - 27.06 = 4.03 \text{ volts (maximum).}$$

This is equivalent to 102,500 calories per gram molecule and is only slightly larger than the values secured by other methods. Langmuir² secured 84,000 calories, Isnardi³ 100,000 calories and Wohl⁴ 95,000 calories.

The moment of inertia of the normal state of the hydrogen molecule ion assuming that this is the first vibration state is about what should be expected from the moment of inertia of the excited hydrogen molecule as calculated from the Fulcher bands of hydrogen. The moment of inertia of the normal ion is 2.60×10^{-41} g. cm.², while the moment of inertia of the hydrogen molecule as calculated from the first Fulcher bands⁵ is about 1.86×10^{-41} g. cm.² The Bohr⁶ model of the hydrogen molecule ion has a moment of inertia of 7.05×10^{-41} g. cm.² and the Pauli-Niessen⁷ model, 72.0×10^{-41} g. cm.²

There are four points of agreement between the theory and the experimental data. The theoretical calculation of the two empirical formulae (6) and (7) may be regarded as two independent points of agreement. The calculation of the heat of dissociation of hydrogen, though only approximate, checks the experimental data fairly well and the value calculated is the larger as is to be expected. Finally the moment of inertia calculated for the hydrogen molecule ion is only slightly larger than that of the excited hydrogen molecule as calculated from band spectra, and shows far better agreement with the expected value than either the Bohr or Pauli-Niessen models of the ion.

The theory, however, does not agree with a large part of the ionizing potential data on hydrogen. Most observers agree on placing the ionizing potential of hydrogen at about 16 volts instead of <14.80 volts. However, it seems that agreement between so simple a theory and even one piece of experimental work claiming such a high precision (a few hundredths of a volt) is of some interest.

The theory predicts that there should be an ultra-violet spectrum belonging entirely to the hydrogen molecule ion and free from the spectrum of the hydrogen molecule in the region between about 850Å and 741Å.

Further work is being done on the calculation of the rotational and vibrational states of the nuclei of the hydrogen molecule ion with the object of testing the theory with the spectroscopic data on the many lined spectrum of hydrogen.

¹ A. R. Olson and G. Glockler, *Proc. Nat. Acad. Sci.*, 9, 122 (1923).

² Irving Langmuir, *J. Amer. Chem. Soc.*, 37, 417 (1915).

³ T. Isnardi, *Z. Elektrochemie*, 21, 405 (1915). Wohl corrected a slight error of calculation in Isnardi's work. See following reference.

⁴ K. Wohl, *Ibid.*, 30, 49 (1924).

⁵ H. S. Allen, *Proc. Roy. Soc.*, 106A, 69 (1924).

⁶ The energy and dimensions of the Bohr model have been given by Sommerfeld in his book on *Atombau und Spektrallinien*, 3rd Edition, Friedr. Vieweg & Sohn. See appendix 14.

⁷ W. Pauli, *Ann. Physik*, 68, 177 (1922). K. F. Niessen, *Ibid.*, 70, 129 (1923).