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EXPERIMENTAL TESTS OF THE  
QUANTUM THEORY OF  
MOLECULAR HYDROGEN

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## EXPERIMENTAL TESTS OF THE QUANTUM THEORY OF MOLECULAR HYDROGEN (\*)

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SUMMARIVM — Novae constantium molecularum  $H_2$ , HD et  $D_2$ , in suo statu primario seu fundamentalis, mensiones, per experimenta factae, congruunt omnino cum theoreticis computationibus. Alia confirmatio autem obtenta est ex spectro continuo  $H_2$  et  $D_2$ , quod nuper perspectum est.

### A. INTRODUCTION

Over forty years ago Professor DIRAC made the often-quoted statement [1] that the whole of chemistry is contained in the wave equation. Unfortunately an actual test of this statement is beset with considerable difficulties because of the mathematical complications of the solution of the wave equation in all but the simplest cases. The work to be discussed

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here had the aim of testing Professor DIRAC'S statement for the simplest chemical system, the  $H_2$  molecule and its isotopes, up to a higher degree of accuracy than had been done before. This was done by comparing new experimental values of various molecular constants, viz. ionization potential, dissociation energy, internuclear distances, rotational and vibrational quanta, with those derived from recent ab initio calculations.

The results of this comparison, as expected by DIRAC, show a most gratifying accord between theory and experiment within the present accuracy of calculation and measurement. Although one of the aims of the present work was the determination of quantum electrodynamics effects (Lamb shifts) on the hydrogen molecule, the present accuracy is unfortunately not sufficient to determine these effects, which recent theoretical studies have predicted to be much smaller than originally expected.

## B. EARLY WORK ON $H_2$ AND $H_2^+$

### (a) *Theory*

The earliest calculations of the dissociation energy of the  $H_2^+$  ion were carried out by BURRAU [2] in 1927. They were followed by the work of GUILLEMIN and ZENER [3], TELLER [4], HYLLERAAS [5], JAFFÉ [6], SANDEMAN [7] and JOHNSON [8]. These studies led to the value

$$D_0^0(H_2^+) = 21345 \pm 20 \text{ cm}^{-1}$$

which, until a few years ago, was the accepted theoretical value.

The ground state of the  $H_2$  molecule and its dissociation energy was first calculated by HEITLER and LONDON [9] in 1927. Their work was refined by WANG [10], ROSEN [11], WEINBAUM [12], and, finally, by the monumental work of JAMES and COOLIDGE [13] in 1933, carried out before the development of modern computers. It resulted in the value

$$D_0^0(H_2) = 36104 \pm 100 \text{ cm}^{-1}$$

which, until 1960, was considered to be the best theoretical value.

The ionization potential of the  $H_2$  molecule follows from  $D(H_2)$  and  $D(H_2^+)$  from the simple equation

$$(1) \quad \text{I.P.}(H_2) = \text{I.P.}(H) + D_0^0(H_2) - D_0^0(H_2^+)$$

and, with the values for  $D_0^0(H_2)$  and  $D_0^0(H_2^+)$  given and  $\text{I.P.}(H) = 109678.8 \text{ cm}^{-1}$ , becomes

$$\text{I.P.}(H_2) = 124438 \pm 100 \text{ cm}^{-1} .$$

Another important early theoretical result was the calculation of the repulsive state of  $H_2$  resulting from two H atoms when their spins are parallel, by HEITLER and LONDON [9] and JAMES, COOLIDGE and PRESENT [14]. As was first suggested by WINANS and STUECKELBERG [15] this state represents the lower state of the continuous spectrum of hydrogen in the visible and near ultraviolet regions, a suggestion that has been confirmed in detail by the calculations of COOLIDGE, JAMES and PRESENT [16, 17].

(b) *Experimental*

WITMER [18] in 1926 was the first to give a fairly good value for the dissociation energy of the neutral  $H_2$  molecule from its emission spectrum in the vacuum ultraviolet. DIEKE and HOPFIELD [19] used the edge of a continuous absorption in the vacuum ultraviolet to determine the dissociation energy, a method that was greatly refined and made more precise by BEUTLER [20]. From the potential diagram, Fig. 1, it is clear that the dissociation energy is given by

$$(2) \quad D_0^0(H_2) = \nu_{\text{lim}} - E(H, n = 2) ,$$

where  $\nu_{\text{lim}}$  is the observed limit of continuous absorption for zero rotation ( $J = 0$ ) and  $E(H, n = 2)$  is the excitation energy of the H atom in the  $n = 2$  state. The value that BEUTLER obtained was

$$D_0^0(H_2) = 36116 \pm 6 \text{ cm}^{-1} .$$

The ionization potential of the hydrogen molecule was first obtained by an extrapolation of a very short Rydberg series by RICHARDSON [21] and later, more precisely, from preionization and predissociation data by BEUTLER and JÜNGER [22]. They obtained

$$\text{I.P.}(H_2) = 124429 \pm 13 \text{ cm}^{-1}$$

If this value is combined with the experimental value for  $D_0^0(H_2)$  according to eq. (1) one obtains for the  $H_2^+$  ion

$$D_0^0(H_2^+) = 21366 \pm 15 \text{ cm}^{-1}$$

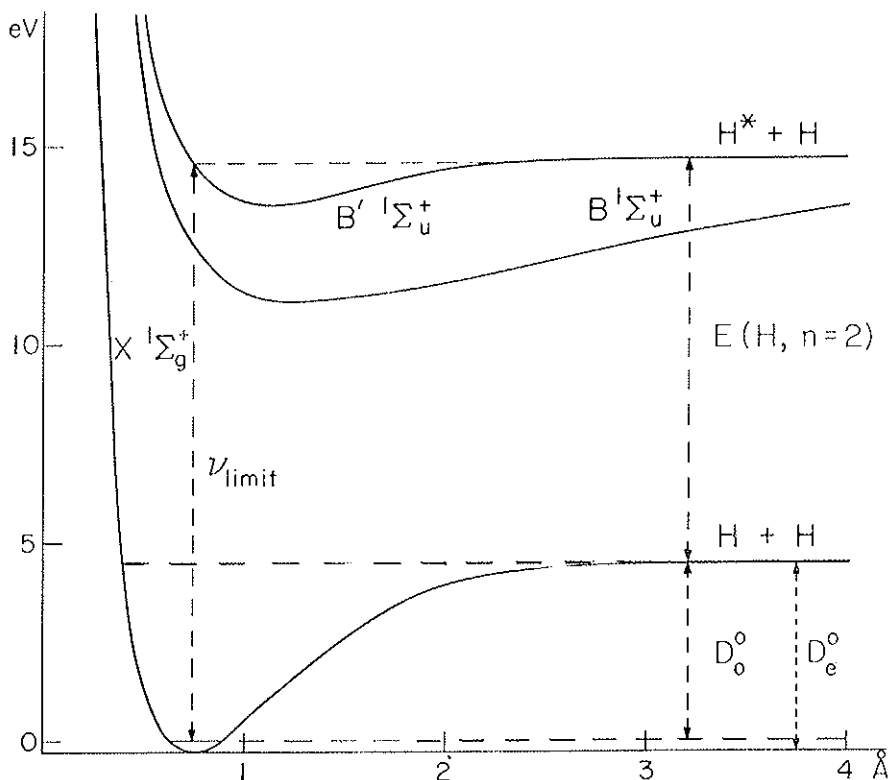


FIG. 1 — Potential energy diagram of  $H_2$  explaining the relation of the absorption limit to the dissociation energy of the ground state. In addition to the ground state  $^1\Sigma_g^+$  the two lowest  $^1\Sigma_u^+$  states are shown. The observed absorption continuum corresponds mainly to a transition to the  $B' ^1\Sigma_u^+$  state.

This was the experimental situation until 1960 when HERZBERG and MONFILS [23] repeated BEUTLER'S work for the three isotopes  $H_2$ ,  $HD$  and  $D_2$  with much higher resolution and obtained the values given in the second column of Table I. By adding the zero point energies the values for  $D_e$  (dissociation energies referred to the equilibrium position, see Fig. 1) in the third column of Table I were obtained which, when

extrapolated to infinite mass, yield the value in the fourth row of Table I. At the same time KOLOS and ROTHAAAN [24] had carried out new calculations of the potential function of  $H_2$  assuming fixed nuclei and had obtained the  $D_e^0$  value given in the last row of Table I, which agrees in a very satisfactory way with the experimental value.

TABLE I. — *Dissociation energies (1960).*

	$D_0^0$ (cm <sup>-1</sup> )	$D_e^0$ (cm <sup>-1</sup> )
H <sub>2</sub>	36113.6 ± 0.3	38292.3 ± 0.5
HD	36399.9 ± 1.0	38290.3 ± 1.5
D <sub>2</sub>	36743.6 ± 0.5	38290.8 ± 0.7
H <sub>2</sub> <sup>∞</sup>	—	38287.0 ± 0.8
calc.	(KOLOS and ROTHAAAN)	38286.9

### C. RECENT WORK ON THE DISSOCIATION ENERGIES OF H<sub>2</sub>, HD AND D<sub>2</sub>

Unfortunately, as the theoretical calculations were improved (KOLOS and WOLNIEWICZ [25]) a systematic discrepancy arose since, by the variation principle, the theoretical energies upon improvement of the approximation go down, that is, the dissociation energies increase. The new theoretical work produced, moreover, directly values for  $D_0^0$  rather than  $D_e^0$ . The discrepancies between theory and experiment that arose in this way are shown in Table II.

In order to ascertain the cause of these discrepancies a new study of the far ultraviolet spectrum of  $H_2$ , HD and  $D_2$  was undertaken (HERZBERG [26]) with two important improvements: (1) The spectra were taken with our 10 m vacuum spectrograph instead of the 3 m instrument used for the 1960 measurements, leading to an improvement in resolving power by a factor of three, and (2) the spectra were taken at liquid nitrogen temperature in order to remove many disturbing and overlapping lines arising from rotational levels other than  $J = 0$ .

TABLE II. — *Observed and calculated dissociation energies (1968).*

	$D_0^0$ observed [23]	$D_0^0$ calculated [25]
$H_2$	$36113.6 \pm 0.3$	36117.4
HD	$36399.9 \pm 1.0$	36405.2
$D_2$	$36743.6 \pm 0.5$	36748.0
	$cm^{-1}$	$cm^{-1}$

Figs. 2, 3 and 4 show sections of the new spectra for  $H_2$ ,  $D_2$  and HD. In  $H_2$  there are two  $J = 0$  lines which overlap the absorption limit. These had been unresolved in the previous work which therefore had given too small a value for the limit. In  $D_2$ , in the previous work the  $J = 0$  limit had not been observed and it had been necessary to extrapolate from the  $J = 1$ ,  $J = 2$  limits. In the new work, at liquid nitrogen temperature the  $J = 0$  limit of  $D_2$  is clear and not overlapped by any line and can be accurately measured (see Fig. 3). In HD two limits are observed (Fig. 4)



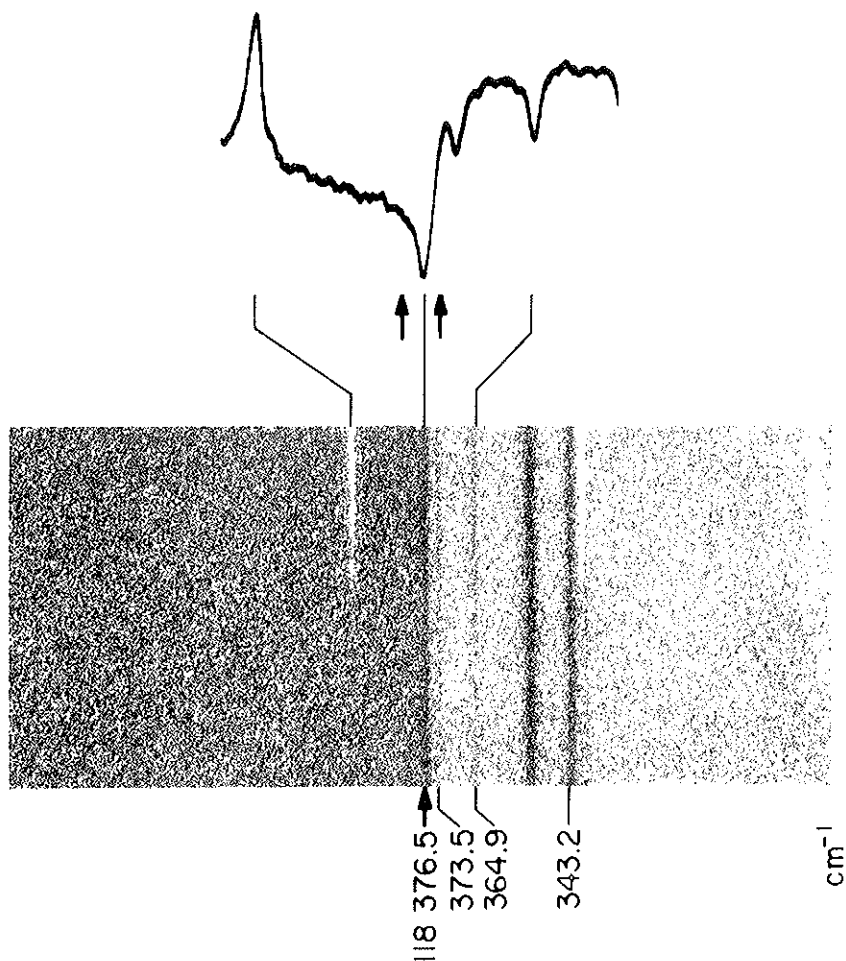


FIG. 2 — The  $J'' = 0$  absorption limit of  $H_2$  near  $844.8 \text{ \AA}$ . The limit is marked by an arrow in the spectrogram. In the enlarged photometer curve at the top it must lie between the two vertical arrows.

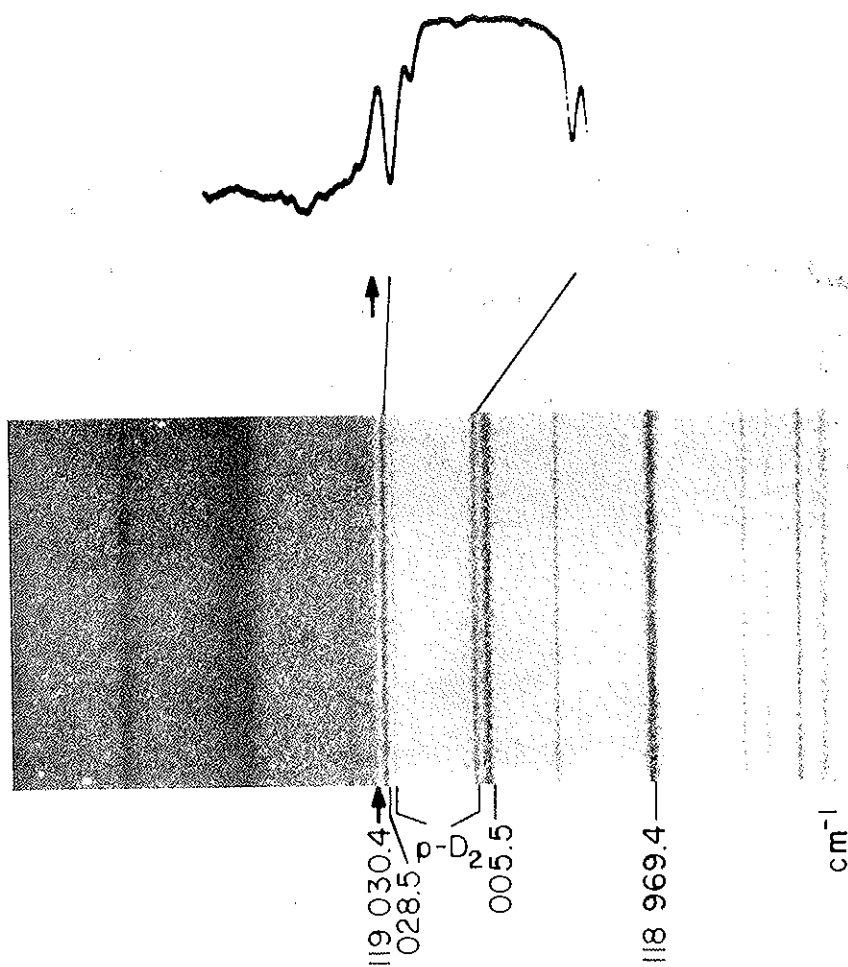


FIG. 3 — The  $J'' = 0$  absorption limit of  $D_2$  near  $840.1 \text{ \AA}$ .

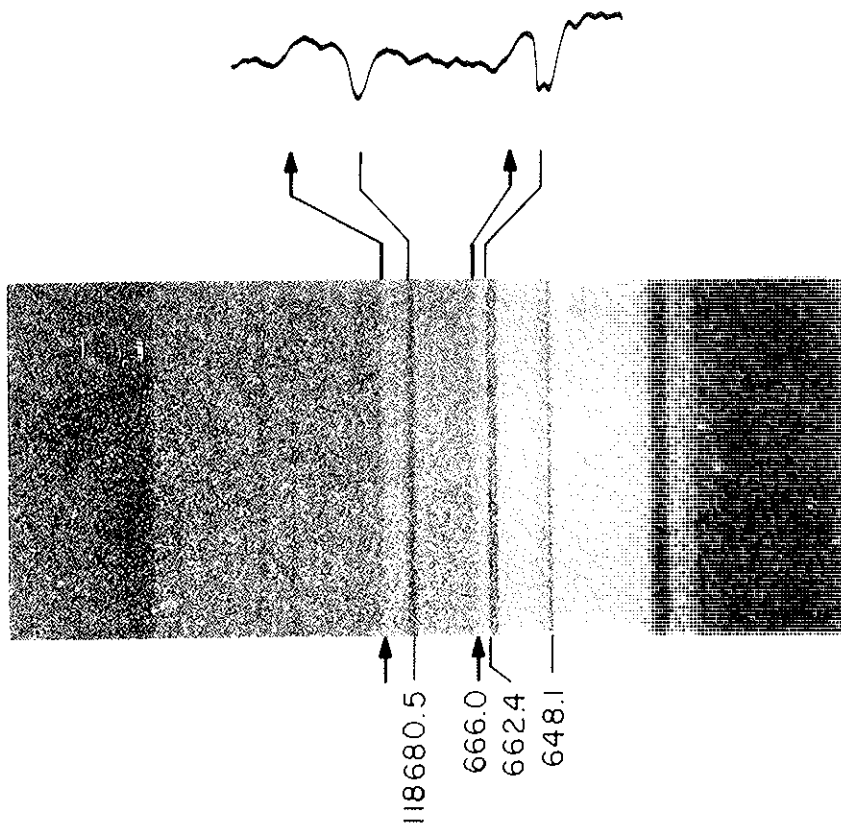


FIG. 4 — The  $J'' = 0$  absorption limits of HD near 842.6 Å. The two limits are marked by arrows.

which correspond to dissociation at the limit into either  $H + D^*$  or  $D + H^*$ .

In Table III the new dissociation energies obtained from the observed limits after a very small correction for the rotational barrier (of the order of  $0.2 \text{ cm}^{-1}$ ) are compared with the latest theoretical values. There is still a very small difference between theory and experiment but it is not much

larger than the experimental error ( $\pm 0.4 \text{ cm}^{-1}$ ) and an improvement of the theoretical calculations would now make a change in the right direction. It may be mentioned that the predicted Lamb shift is only  $-0.2 \text{ cm}^{-1}$  which is well within the estimated error limits of the observations and therefore cannot be determined.

#### D. VIBRATIONAL AND ROTATIONAL LEVELS OF THE GROUND STATE

The Raman data of STOICHEFF [27] still give the best values for the first two rotational constants  $B_0$  and  $B_1$ , as well as for the first vibrational quantum  $\Delta G\left(\frac{1}{2}\right)$  of  $\text{H}_2$ , HD and  $\text{D}_2$ . The quadrupole spectrum of  $\text{H}_2$ , first investigated by HERZBERG [28] and later studied under higher resolution by RANK and his collaborators [29, 30], supplies corresponding constants for  $v = 2$  and  $v = 3$ . For  $\text{D}_2$  the quadrupole spectrum has not been observed, but recently Dr. H. BREDOHL and I [31] have determined from the LYMAN bands and WERNER bands in the ultraviolet the rotational constants and the vibrational intervals for all the vibrational levels of the ground state with an accuracy comparable to that of STOICHEFF. This study was similar to an earlier study by HERZBERG and HOWE [32] of the higher vibrational levels of  $\text{H}_2$  not covered by the study of the Raman and quadrupole spectra.

For HD, apart from STOICHEFF's Raman spectrum, the dipole infrared spectrum has been studied by DURIE and HERZBERG [33], giving rotational and vibrational constants up to  $v = 4$ . The higher vibrational intervals have been observed with less accuracy from resonance series observed in mixtures of argon and HD by TAKEZAWA, INNES and TANAKA [34].

KOLOS and WOLNIEWICZ [25], in addition to the dissociation energies, have also derived from the theoretical potential function, values for the vibrational intervals  $\Delta G\left(v+\frac{1}{2}\right)$  of  $\text{H}_2$ ,

TABLE III. — *Calculated and observed dissociation energies of H<sub>2</sub>, HD and D<sub>2</sub> (1970).*

	Theor. (*)	Obs. [26]
$D_0^0$ (H <sub>2</sub> )	36117.9	< 36118.3 > 36116.3
$D_0^0$ (HD)	36405.5	{ 36406.6 36405.8
$D_0^0$ (D <sub>2</sub> )	36748.2 cm <sup>-1</sup>	36748.9 ± 0.4 cm <sup>-1</sup>

(\*) Including non-adiabatic corrections according to BUNKER [44].

HD and D<sub>2</sub>. In addition, they have derived expectation values of  $r^{-2}$  (in atomic units) which are readily converted to predicted values of the rotational constants

$$B_v = \frac{h}{8\pi^2 c \mu} \left[ \frac{1}{r^2} \right]_{\text{average}}$$

In Table IV and V the observed  $\Delta G$  values are compared with the theoretical ones for H<sub>2</sub> and D<sub>2</sub> respectively. In all cases there is a systematic discrepancy which for low  $v$  for H<sub>2</sub> is of the order of 0.8 cm<sup>-1</sup>, for D<sub>2</sub> of the order of 0.4 cm<sup>-1</sup>. In Fig. 5 the deviations are represented graphically, including the data for HD.

Another way of presenting this discrepancy is to plot the differences between the observed and calculated energies of

TABLE IV. — *Vibrational quanta in the ground state of H<sub>2</sub> [32].*

$v$	$\Delta G \left( v + \frac{1}{2} \right)$	
	obs.	theor.
0	4161.14	4162.06
1	3925.98	3926.64
2	3695.24	3696.14
3	3468.01	3468.68
4	3241.56	3242.24
5	3013.73	3014.49
6	2782.18	2782.82
7	2543.14	2543.89
8	2292.96	2293.65
9	2026.26	2026.81
10	1736.66	1737.13
11	1414.98	1415.54
12	1049.18	1048.98
13	621.96	620.16

the levels (rather than their intervals). This is done in Fig. 6. As the curves show, the magnitude of the discrepancy first increases with  $v$  but then fairly suddenly turns and decreases. According to POLL and KARL [35] the discrepancy between observed and calculated vibrational levels is of the right order of magnitude to be accounted for by the effect of non-adiabatic corrections, but a quantitative calculation of these effects has not yet been made.

TABLE V. — *Vibrational quanta in the ground state of D<sub>2</sub> [31].*

$v$	$\Delta G \left( v + \frac{1}{2} \right)$	
	obs.	theor.
0	2993.56 <sup>a</sup>	2993.96
1	2873.6 <sup>b</sup>	2874.82
2	2757.18	2757.79
3	2642.20	2642.40
4	2528.08	2528.21
5	2414.52	2414.75
6	2301.20	2301.45
7	2187.51	2187.72
8	2072.61	2072.98
9	1956.14	1956.46
10	1836.87	1837.24
11	1714.00	1714.48
12	1586.39	1586.83
13	1452.52	1452.84
14	1310.84	1311.23
15	1159.27	1159.59
16	995.14	995.67
17	815.43	815.66
18	615.72	615.60
19	391.15	390.59
20	141.69	

<sup>a</sup> From STOICHEFF [27].

<sup>b</sup> From TAKEZAWA, INNES and TANAKA [34].

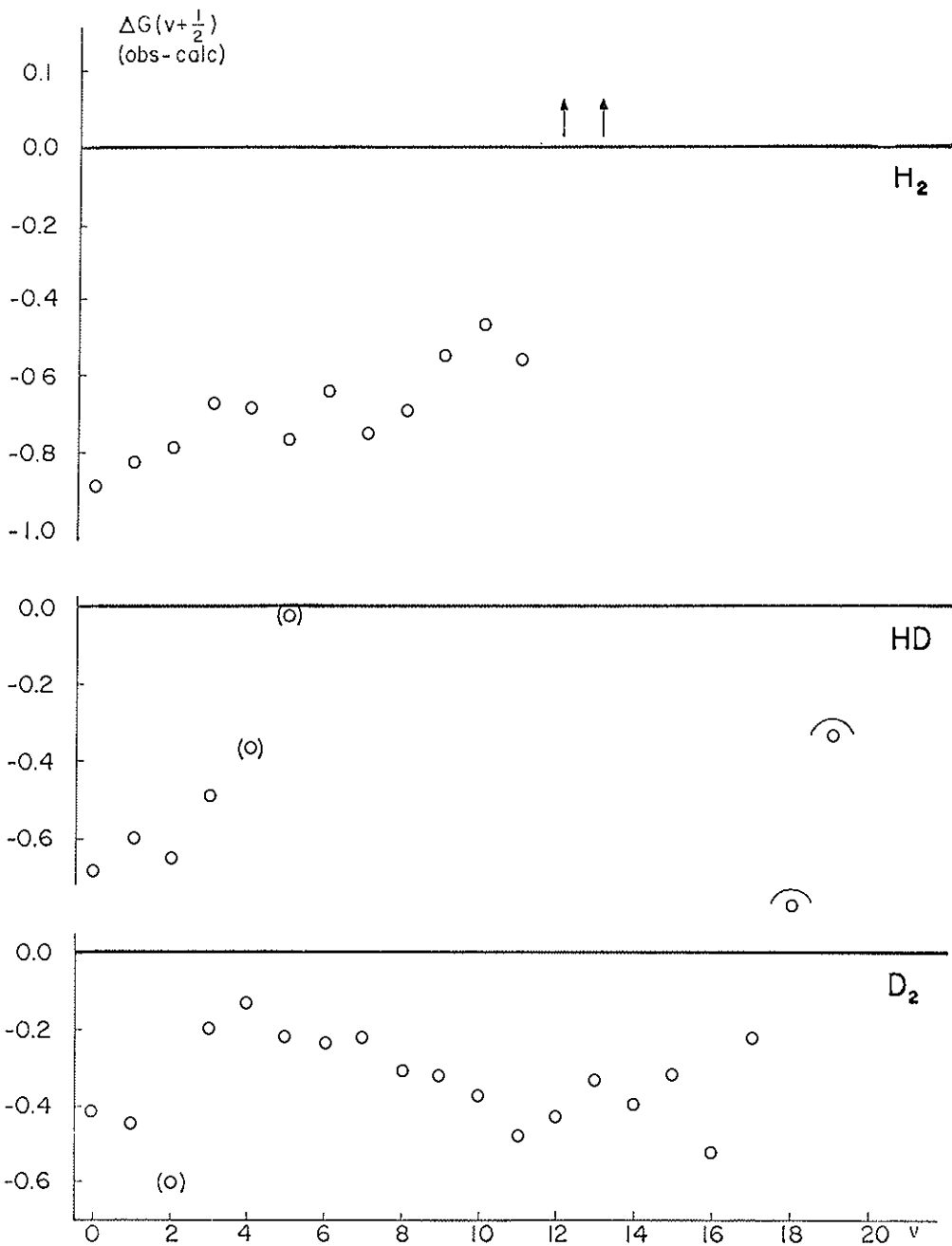


FIG. 5 — Deviations of observed vibrational quanta,  $\Delta G\left(v + \frac{1}{2}\right)$ , of  $H_2$ ,  $HD$  and  $D_2$  from those obtained from theory.



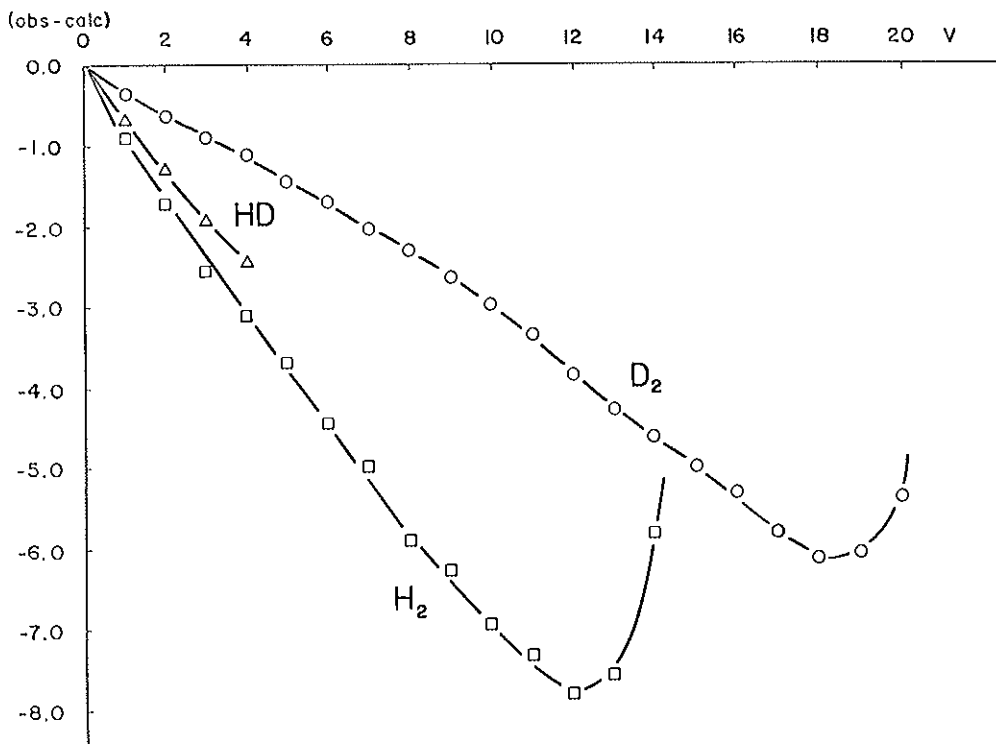


FIG. 6 — Deviations of observed vibrational levels  $G(v)$  of  $H_2$ , HD and  $D_2$  from those obtained from theory.

In Fig. 7 the differences between the observed and calculated rotational constants are plotted (<sup>1</sup>). Again, for  $H_2$  and  $D_2$  the observed values are systematically lower than the calculated values. The effect is small and just outside the limit of accuracy of the observations. For HD the scatter of the

(<sup>1</sup>) The conversion factor used in eq. (3) was  $60.1995/\mu$  where  $\mu$  is the reduced (nuclear) mass in atomic mass units. Recent improvements in the value of the atomic constants (TAYLOR, PARKER and LANGENBERG [49]) would change this factor to  $60.2011/\mu$ , resulting in a small increase in the magnitude of the discrepancies.

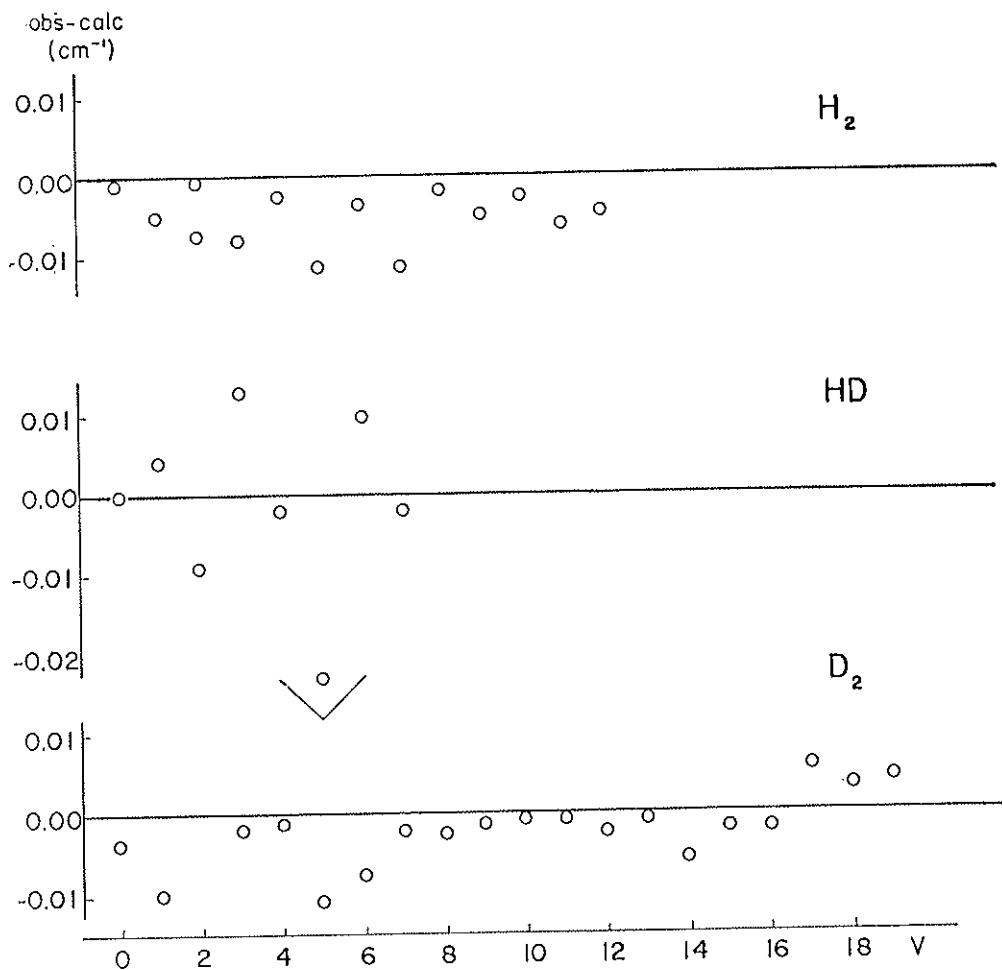


FIG. 7 — Deviations of observed rotational constants  $B_v$  of  $H_2$ , HD and  $D_2$  from those obtained from theory [see foot note (1) on p. 16].

observations is greater than the expected effect would be. It must be assumed that the slight systematic differences for  $\text{H}_2$  and  $\text{D}_2$  (of the order of  $0.005 \text{ cm}^{-1}$ ) are again due to the effect of non-adiabatic corrections.

Another way of comparing theory and experiment is by way of the equilibrium constants  $r_e$ ,  $B_e$  and  $\omega_e$ . In view of certain corrections which are difficult to evaluate we shall not consider these constants in detail here but only mention that if one disregards all corrections and uses the apparent  $B_e$  values at their face values one obtains "observed"  $r_e$  values of  $0.74139 \text{ \AA}$  and  $0.74156 \text{ \AA}$  for  $\text{H}_2$  and  $\text{D}_2$  respectively, which should be compared with the theoretical value of the minimum of the KOLOS-WOLNIEWICZ potential of  $0.74140 \text{ \AA}$ .

## E. IONIZATION POTENTIAL AND DERIVED QUANTITIES

### (a) *Rydberg series*

In the spectra of atoms with a  $s^2 \ ^1S$  (or  $s \ ^2S$ ) ground state there is only one Rydberg series, namely,  $n^1P - ^1S$  (or  $n^2P - ^2S$ ). In a molecule with a  $\sigma^2 \ ^1\Sigma^+$  ground state we expect correspondingly two Rydberg series, namely,  $n^1\Pi - ^1\Sigma^+$  and  $n^1\Sigma^+ - ^1\Sigma^+$ . Two such series have indeed been observed for the hydrogen molecule, but until recently only the lowest members had been found.

Near the Rydberg limit the spectrum of hydrogen is extremely complicated because, for each value of the principal quantum number  $n$ , in each of the Rydberg series we have a whole band system with its widely spaced vibrational and rotational structure. A very considerable simplification of the spectrum can be obtained if it is observed at liquid nitrogen temperature, particularly if para-hydrogen is used, since then only the transitions with  $J''=0$  occur. Under these conditions we did observe two series of lines for each value of the

vibrational quantum number  $v'$  of the upper state [36, 37]. For  $v'=1$  this is shown in Fig. 8. It turns out, however, that the two series of a given  $v'$  have slightly different limits because one of them ( $n^1\Sigma$ ) can only correlate with the  $N=0$  level of the ion, while the other ( $n^1\Pi$ ) can only correlate with  $N=2$  of the ion, and these two rotational levels of the ion are approximately  $180\text{ cm}^{-1}$  apart. ( $N$  is the quantum number of the total angular momentum apart from spin).

In Fig. 9 the two series of levels are shown schematically, together with the continuous energy region that extends beyond each of them. It is immediately clear from Fig. 9 that the levels of the  $\Pi$  series which lie above the limit of the  $\Sigma$  series are subject to preionization, and indeed Fig. 8 shows that the corresponding lines are broad and show apparent emission in the way that was first found by BEUTLER [38] for xenon and explained by FANO [39].

In addition to the preionization above the first ionization limit there are perturbations between accidentally coinciding levels of the two series below the limit. For example, the  $n = 20$  level of the second series (Fig. 9) has about the same energy as the  $n = 34$  level of the first series. These perturbations lead to irregularities in the series, which are clearly shown in Fig. 8. They must be fully understood before a reliable extrapolation of the series limit is possible. FANO [40] has developed an elegant theory for these perturbations. Fig. 10a shows a comparison of the observed series plotted as a difference against an ordinary Balmer series  $\left(\frac{R}{n^2}\right)$ . The full lines are calculated from the FANO formulae. One sees clearly the perturbed places in the  $^1\Sigma$  series.

We have also observed the spectrum of orthohydrogen, that is, lines with  $J'' = 1$ . The upper levels of the Q (1) lines form only a single series and are not perturbed. This is seen in Fig. 10b which shows a plot for the Rydberg Q (1) series. To be sure, there is one perturbation in this series:

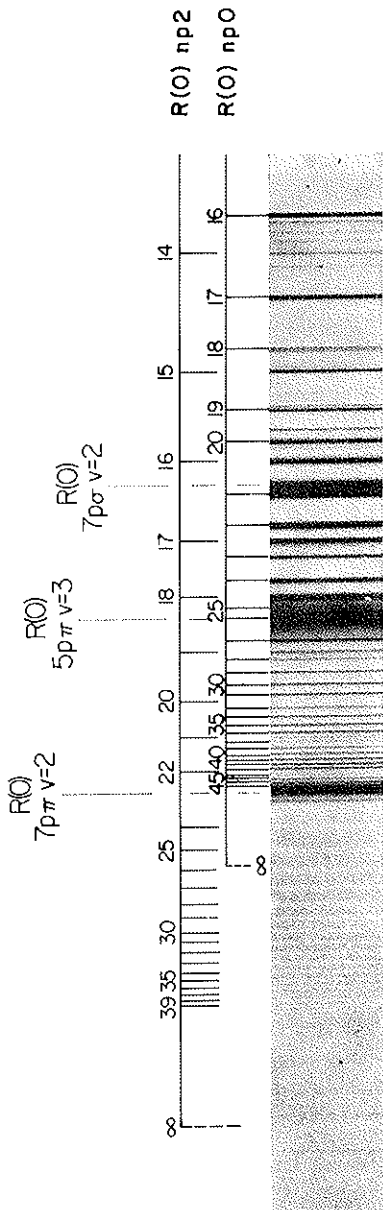


FIG. 8 — Rydberg series of para-hydrogen for  $v' = 1$ . The two series corresponding to  $N = 0$  and  $N = 2$  are marked. The latter appears, above the limit of the former, as an apparent emission series. The three strong lines marked belong to Rydberg series of different  $v'$ .

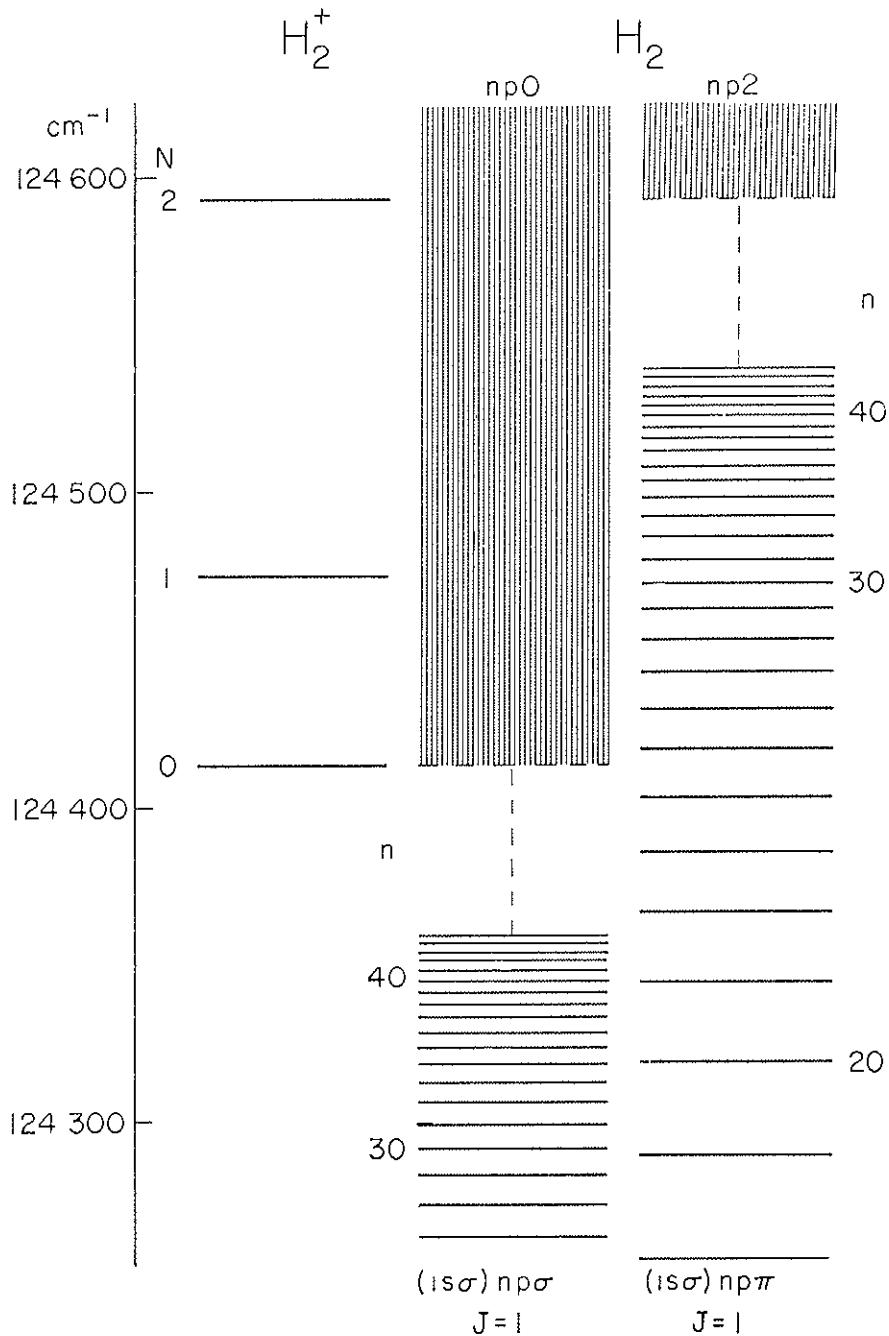


FIG. 9 — Energy levels of the Rydberg electron near the ionization limit ( $v' = 0$ ) and correlation with the rotational levels of  $H_2^+$ . The vertical hatching indicates a continuous energy range.

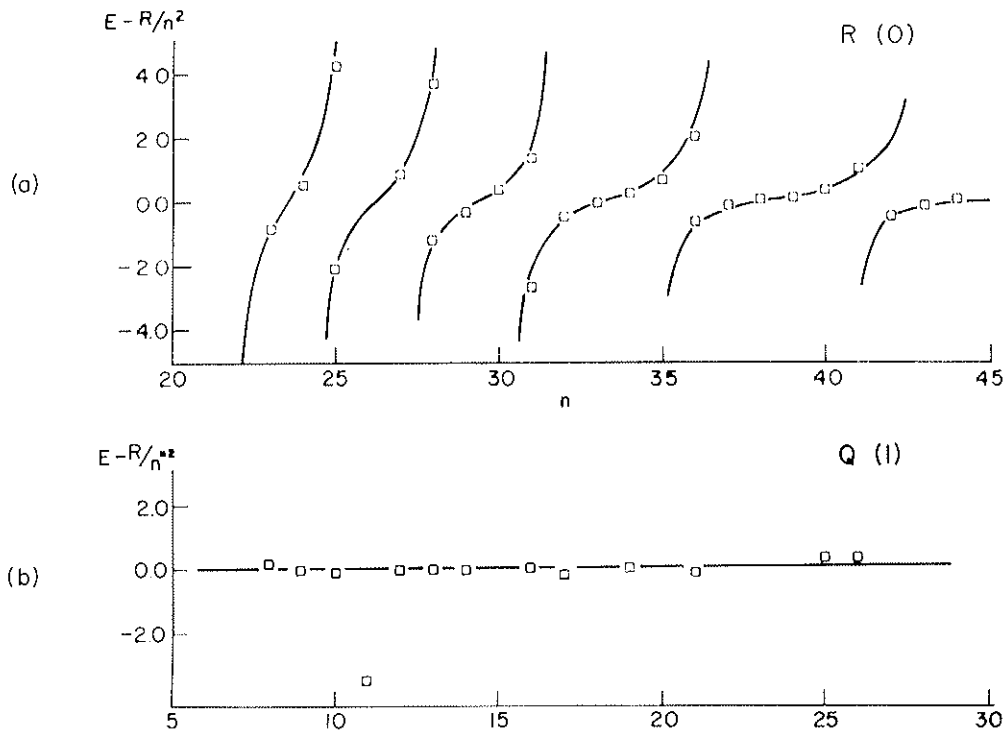


FIG. 10 — Deviation of  $R(0)$  and  $Q(1)$  Rydberg series of  $H_2$  from  $R/n^2$  and  $R/n^{*2}$  respectively for  $v' = 1$ .

it is due to interaction with a  $Q(1)$  level of a different vibrational series. Such perturbations with  $\Delta v \neq 0$  occur also in the para-Rydberg series and complicate matters still further. They have been fully analysed in a recent paper by JUNGEN and myself [37].

The absorption spectra at low temperature had to be taken at a fairly high pressure of helium (40 mm). This pressure was necessary because the source of the continuous background required it and because the hydrogen (of low

pressure) had to be retained in the low temperature absorption tube between light source and slit without solid windows. On account of the fairly high pressure of He there is a shift of the lines of the Rydberg series. The magnitude of this shift was established by comparison with pictures of parahydrogen at room temperature when the hydrogen was at extremely low pressure in the body of the spectrograph. In this way it was found that under the conditions of the low temperature experiments the shift is about  $1 \text{ cm}^{-1}$  independent of  $n$  for  $n > 10$ . The magnitude of the shift is very closely the same as that observed in atomic Rydberg series at the same density. Already in 1934 FERMI [41] had given a very satisfactory theoretical account of this shift.

The various ionization limits obtained for  $v=0, 1, 2$  and  $3$  and corrected to zero pressure are summarized in Table VI. The  $N=1$  limits are referred to the  $J''=0$  level, as are the others, even though the observed  $N=1$  Rydberg limits are at longer wavelengths because they originate from the  $J''=1$  level.

TABLE VI. — *Limits of Rydberg series above  $v''=0, J''=0$ .*

$v$	$N=0$	$N=1$	$N=2$	$N=4$
0	124417.2	124476.0	124591.5	
1	126608.4	126664.2	126773.6	127152.2
2	128672.6	128724.8	128828.0	129185.7
3	130613.4	130662.3	130760.9	



*(b) Ionization potential*

The Rydberg limit for  $N=0$  and  $v=0$  corresponds to the ionization potential of the  $\text{H}_2$  molecule, that is,

$$\text{I.P.}_{\text{obs.}}(\text{H}_2) = 124417.2 \pm 0.4 \text{ cm}^{-1}$$

which may be compared with the latest theoretical value (HUNTER and PRITCHARD [42], JEZIORSKI and KOLOS [43], BUNKER [44])

$$\text{I.P.}_{\text{theor.}}(\text{H}_2) = 124417.3 \text{ cm}^{-1} .$$

It is seen that the agreement is most satisfactory. The predicted Lamb shift (which is included in the theoretical value given) is  $0.33 \text{ cm}^{-1}$ . In view of the estimated error of the observed value the presence of a Lamb shift cannot be experimentally established from the present observations.

It is interesting to note that the ionization potentials of  $\text{D}_2$  and  $\text{HD}$  recently determined by TAKEZAWA [45] and TAKEZAWA and TANAKA [46] give equally good agreement only after a pressure shift correction is made, similar to the one for  $\text{H}_2$ . One then finds

$$\text{I.P.}_{\text{obs.}}(\text{D}_2) = 124745.6 \pm 0.6 \text{ cm}^{-1}$$

$$\text{I.P.}_{\text{obs.}}(\text{HD}) = 124568.5 \pm 0.6 \text{ cm}^{-1}$$

while the theoretical values are

$$\text{I.P.}_{\text{theor.}}(\text{D}_2) = 124745.2 \text{ cm}^{-1}$$

$$\text{I.P.}_{\text{theor.}}(\text{HD}) = 124568.0 \text{ cm}^{-1}$$

(c) *The dissociation energy of the molecular ion*

From the ionization potentials and the dissociation energies given earlier we obtain, according to eq. (I), the following values for the dissociation energies of the ions:

$$D_0^0{}_{\text{obs.}}(\text{H}_2^+) \leq 21379.9 \pm 0.4 \text{ cm}^{-1}$$

$$D_0^0{}_{\text{obs.}}(\text{D}_2^+) = 21711.9 \pm 0.6 \text{ cm}^{-1}$$

$$D_0^0{}_{\text{obs.}}(\text{HD}^+) = 21516.1 \pm 0.6 \text{ cm}^{-1} .$$

These values may be compared with the theoretical values

$$D_0^0{}_{\text{theor.}}(\text{H}_2^+) = 21379.3 \text{ cm}^{-1}$$

$$D_0^0{}_{\text{theor.}}(\text{D}_2^+) = 21711.6 \text{ cm}^{-1}$$

$$D_0^0{}_{\text{theor.}}(\text{HD}^+) = 21516.3 \text{ cm}^{-1}$$

which are considered to be accurate to  $\pm 0.2 \text{ cm}^{-1}$ . That the agreement is again very satisfactory is not surprising since  $D_0^0(\text{H}_2^+)$  is determined by  $D_0^0(\text{H}_2)$  and I.P. ( $\text{H}_2$ ) and for both of the latter very good agreement between theory and experiment was found. The theoretical Lamb shift for  $D_0^0(\text{H}_2^+)$  is only  $0.2 \text{ cm}^{-1}$ .

(d) *Rotational levels of  $\text{H}_2^+$* 

The series limits given in Table VI supply several rotational and vibrational levels of  $\text{H}_2^+$ . These are compared with theoretical values of HUNTER and PRITCHARD [42] in Table VII. It is seen that again the agreement between theory

TABLE VII. — *Observed and calculated vibrational and rotational levels in the ground state of H<sub>2</sub><sup>+</sup>.*

	obs.	calc.
$\Delta G (1/2)$	2191.2	2191.2
$\Delta G (3/2)$	2064.2	2063.9
$\Delta G (5/2)$	1940.8	1941.0
$F (1) - F (0)$		
$v = 0$	58.8	58.2
$v = 1$	55.8	55.2
$v = 2$	52.2	52.2
$v = 3$	48.9	49.3
$F (2) - F (0)$		
$v = 0$	174.3	174.2
$v = 1$	165.2	165.1
$v = 2$	155.4	156.2
$v = 3$	147.5	147.6

and experiment is very satisfactory. The observed rotational and vibrational levels are not sufficient to obtain reliable values for the equilibrium constants of H<sub>2</sub><sup>+</sup> because higher power terms in the energy formulae, which cannot be determined from the few available levels, are quite significant in such a light molecule. However, using the standard formulae one obtains from the observed energy levels an equilibrium

internuclear distance of  $1.052_3 \text{ \AA}$ , while the theoretical value is  $1.05687 \text{ \AA}$ .

#### F. PREDICTED AND OBSERVED CONTINUOUS SPECTRA

As already mentioned, the ordinary continuous spectrum of hydrogen extending from 5000 to  $1700 \text{ \AA}$  is well-known to be due to the transition  $a \ ^3\Sigma_g^+ - b \ ^3\Sigma_u^+$ . The lower state is the HEITLER-LONDON repulsive state arising from two hydrogen atoms with parallel spin. COOLIDGE, JAMES and PRESENT [16, 17] have calculated the intensity distribution in the continuum from first principles and have found excellent agreement with the observed distribution.

Recently a new continuum of hydrogen was observed in our laboratory which extends from  $1600$  to  $1400 \text{ \AA}$  and consists of several broad maxima, as shown in Fig. 11. After various unsuccessful attempts to account for this con-

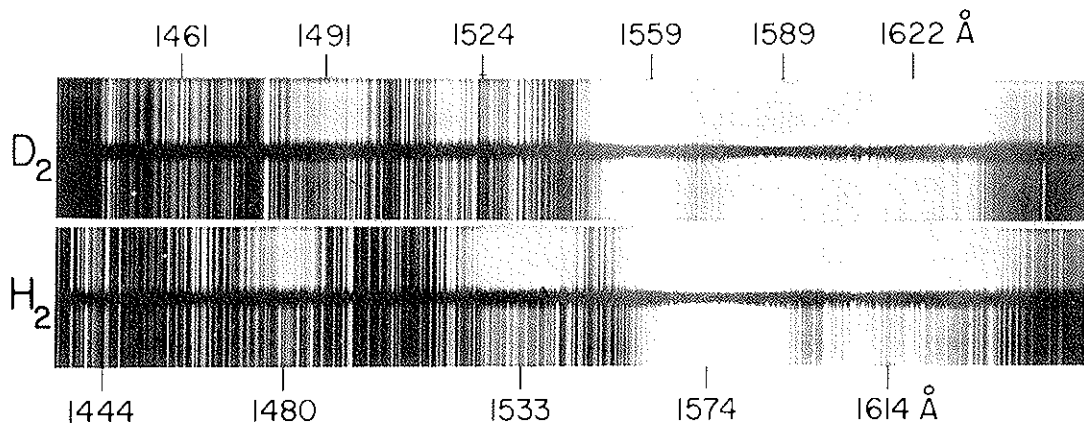


FIG. 11 — Emission spectra of  $H_2$  and  $D_2$  in the region  $1650$ - $1440 \text{ \AA}$ . Two spectra with different exposure times are shown for both  $H_2$  and  $D_2$ . The positions of the intensity maxima of the continuum are indicated.

tinuum it was shown by DALGARNO, HERZBERG and STEPHENS [47] that this continuum corresponds to the transition from the  $B\ ^1\Sigma_u^+$  state to the continuum of the  $X\ ^1\Sigma_g^+$  ground state; in other words, that it is part of the Lyman system of hydrogen. If one were to calculate the intensity distribution of the continuous wavefunction by  $\delta$  functions one would not obtain such a fluctuating continuum. It is only when the maxima and minima of the wavefunctions in the continuum are taken into account that this spectrum can be accounted for.

In Fig. 12 the wavefunctions are shown for the upper state  $v' = 9$  and for a lower state in the continuum. It is clear that by varying the energy in the continuum a fluctuating intensity distribution is obtained, as shown in Fig. 13. Such fluctuations were first predicted by CONDON [48] in his second paper on the FRANCK-CONDON principle and have often been referred to as CONDON diffraction bands. If the effect of different vibrational levels in the upper state is superimposed one obtains surprising agreement between theory and observation, as shown in Figs. 14 and 15 for  $H_2$  and  $D_2$  respectively.

The calculations have been carried out only for the lowest rotational level  $J' = 0$ . In this case each vibrational level gives rise to a distribution as given in Fig. 13 with a sharp, short wavelength limit. The observed limits are much less sharp, presumably because several rotational levels are overlapped. If this spectrum could be observed under conditions when only one rotational level is effective very sharp limits should be found which could serve as an independent check of the value of the dissociation energy.

## G. CONCLUSION

I believe that the preceding discussion shows that on the whole there is excellent agreement of the observed data on  $H_2$ , HD and  $D_2$  with theoretical data based on ab initio calcu-

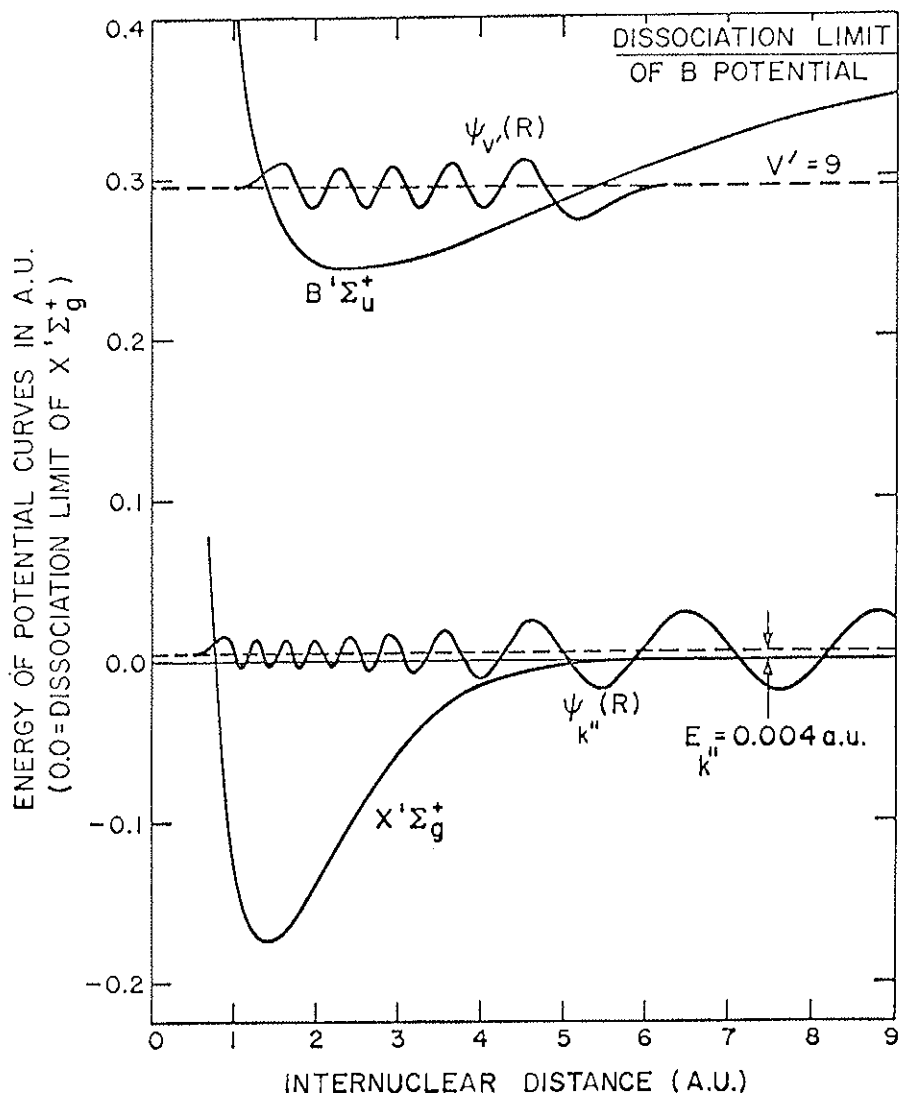


FIG. 12 — Wavefunctions of the  $v' = 9$  level in the  $B^1\Sigma_u^+$  state and of the continuum in the  $X^1\Sigma_g^+$  ground state of  $H_2$  for  $E = 0.004$  a.u. The potential curves in the two states are included.

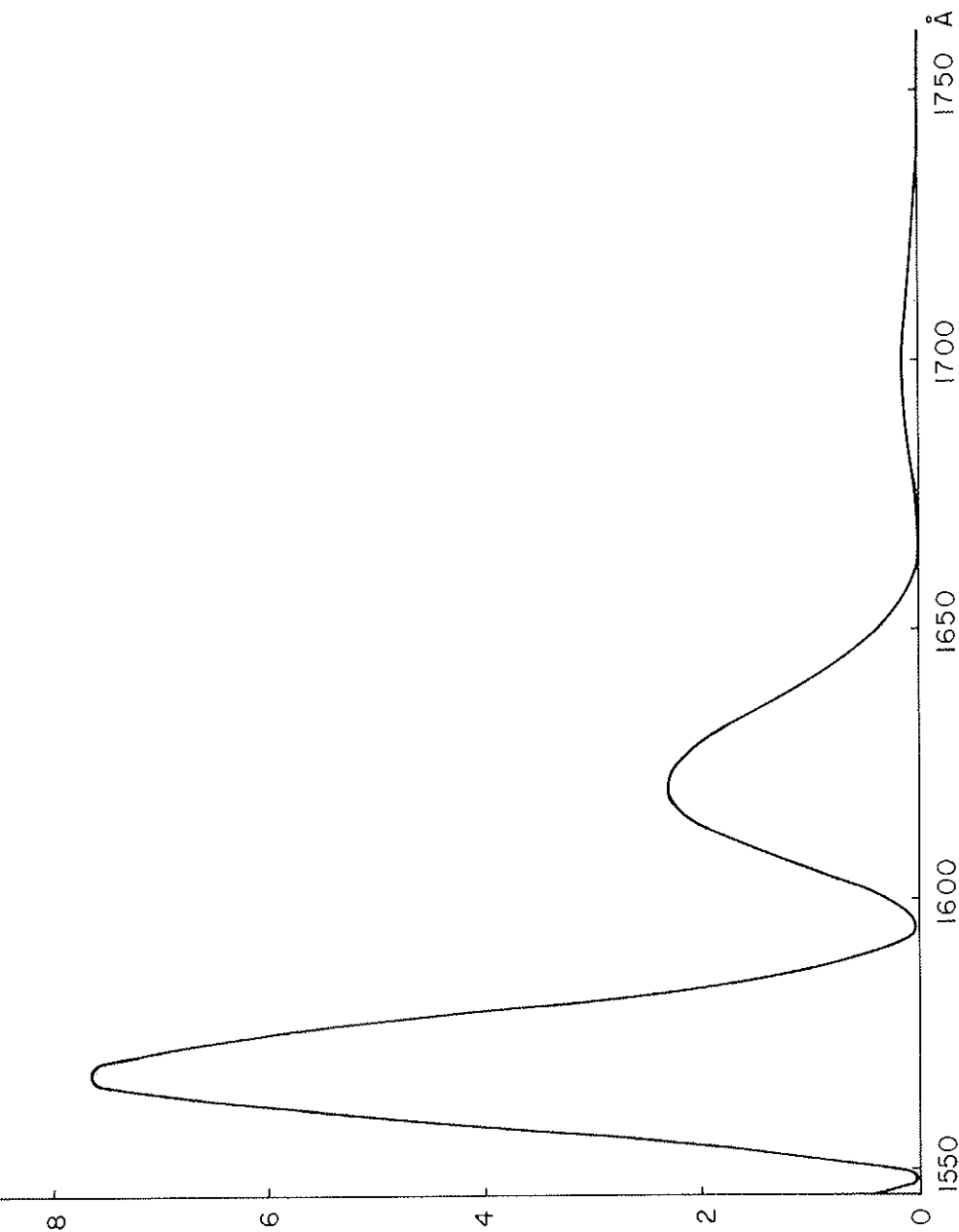


FIG. 13 — Theoretical intensity distribution in the partial emission continuum arising from the  $v' = 9$  level of the  $B \ ^1\Sigma_g^+$  state.

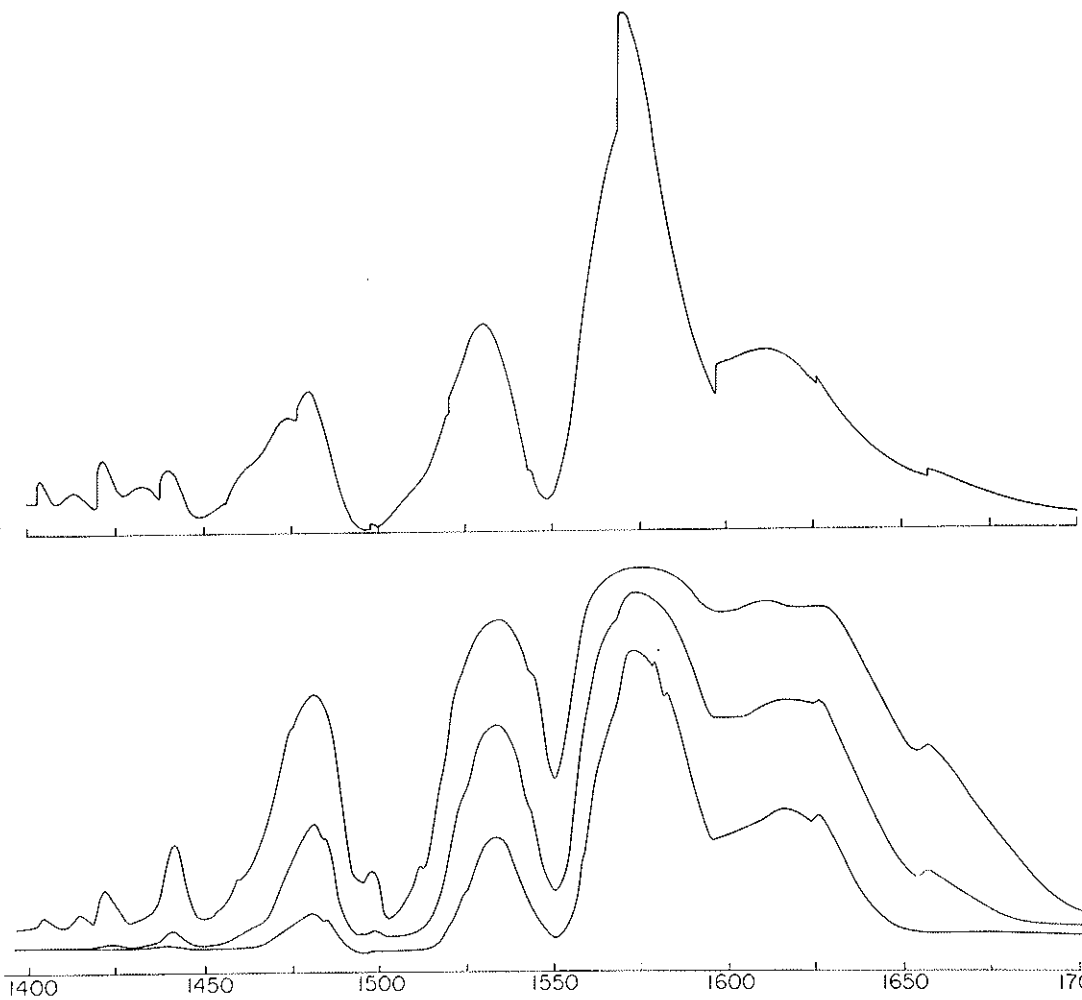


FIG. 14 — Photometer curves (a) and theoretical intensity distribution (b) in the  $\text{H}_2$  continuum between 1700 and 1400 Å. In (a) three curves corresponding to different exposure times are shown in order to bring out both the weak and the strong features. The theoretical curve in (b) refers to zero rotation.



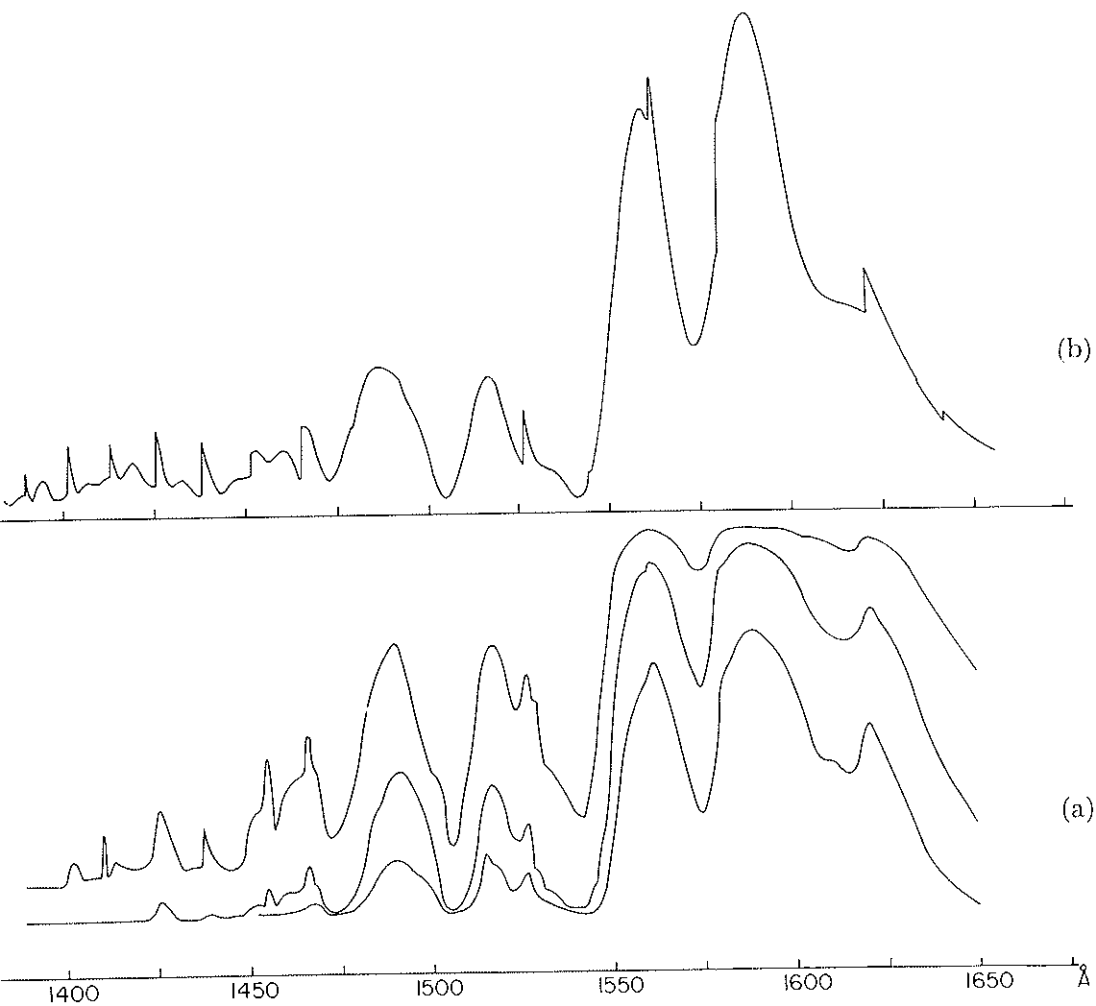


FIG. 15 — Photometer curves (a) and theoretical intensity distribution (b) in the  $D_2$  continuum between 1700 and 1400  $\text{\AA}$ . See caption of Fig. 14.

lations. In Table VIII the quality of the agreement for various constants is summarized. The remaining very small discrepancies must be ascribed partly to non-adiabatic corrections, as mentioned earlier, and partly to error of measurement.

TABLE VIII. — *Summary of the agreement between theory and experiment.*

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I.P.	within 2 ppm
$D_0^0$ (H <sub>2</sub> , HD, D <sub>2</sub> )	within 10 ppm
$D_0^0$ (H <sub>2</sub> <sup>+</sup> , D <sub>2</sub> <sup>+</sup> )	within 10 ppm
$B_v$	within 120 ppm
$B_e$	within 250 ppm
$r_e$	within 150 ppm
$\Delta G$	within 200 ppm
$\omega_e$	within 500 ppm

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