

Metastable Hydrogen Molecules. II. Fine Structure of Parahydrogen

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The fine structure of the $N=2$ rotational level of the $(1\sigma_g, 1\pi_u)c^3\Pi_u$ state of parahydrogen, very probably in the $v=0$ vibrational level, has been measured directly by means of the molecular beam magnetic resonance method. The zero field intervals are: $f(J=2 \leftrightarrow J=1)=4928.003 \pm 0.010$ Mc/sec, $f(J=3 \leftrightarrow J=2)=5898.105 \pm 0.012$ Mc/sec. The spin-spin and spin-orbit interaction constants are in agreement with theoretical predictions based on a simplified hydrogenic model.

INTRODUCTION

RECENTLY,¹ it has been shown that the hydrogen molecule has a metastable electronic state, $c^3\Pi_u$. This discovery makes possible precise measurements of the finer details of the structure of H_2 by the molecular beam magnetic resonance (Rabi) technique.

The present paper is a report on the first direct measurement of the fine structure (fs) of H_2 . It begins with a brief historical account of previous work.

1. HISTORY OF PREVIOUS OBSERVATIONS

One of the outstanding successes of physics is the complete, precise agreement between experiment and theory for the electromagnetic properties of the simplest atomic systems.^{3,4} Of particular interest is the measurement of the fs of hydrogen by Lamb and co-workers to a precision of 0.2 Mc/sec.⁵ This measurement provides the most precise value for the fs constant $\alpha=1/(137.0390 \pm 0.0012)$, a fundamental quantity which enters into the theory of atomic or molecular fs or hyperfine structure (hfs).^{4,5}

Considerable progress has been made in the study of helium, the system of least additional complexity. Since He has two electrons, approximate variational wave functions must be used in theoretical calculations, as opposed to exact wave functions in the case of simpler systems.⁴ However, the precise measurements of the Zeeman effect⁶ of He, $(1s, 2s) ^3S_1$; the ionization po-

tential⁷ of He, $(1s)^2 ^1S$ and $(1s, 2s), ^3S_1$; and the hfs⁸ of He³, 3S_1 all agree with theoretical calculations⁹ within the combined experimental and theoretical uncertainties. It is worth noting that the comparison of the hfs results of reference 8 gives the total electron density at the He nucleus in the 3S_1 state. This quantity, which is a sum of one electron operators, has been calculated⁹ to within a part in 10^5 of the experimental results. This is perhaps the most stringent test to date of variational calculations. The fs of He, $(1s, 2p) ^3P_{2,1,0}$ depends on more complicated two-electron interactions, and thus, may furnish an even stricter test of theory. Measurements of the fs to a precision of 1 part in 10^5 have been reported recently.¹⁰

H_2 consists of two protons and two electrons. Thus, it follows He as the next system of higher complexity. It is the simplest molecular system which has been studied experimentally.¹¹ Recently, digital computer calculations of a variational wave function for the ground state of H_2 by Kolos and Roothaan¹² have made possible predictions of energies and other observable properties¹³ which are in precise agreement with experiment.^{14,15} Thus, it appears possible that a relatively

⁷ G. Herzberg, Proc. Roy. Soc. (London) A248, 309 (1958) and unpublished data mentioned in reference 8.

⁸ J. A. White, L. Y. Chow, C. Drake, and V. W. Hughes, Phys. Rev. Letters 3, 428 (1959) (hfs of He³, 3S_1); R. Novick and E. D. Commins, Phys. Rev. 111, 822 (1958) (hfs of He³⁺, 2^2S_1).

⁹ C. L. Pekeris, Phys. Rev. 115, 1216 (1959).

¹⁰ F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, Phys. Rev. Letters 3, 420 (1959); J. Lifshitz and R. H. Sands, Bull. Am. Phys. Soc. 6, 424 (1961). For theoretical calculations, see G. Araki, M. Ohta, and K. Mano, Phys. Rev. 116, 651 (1959); J. Traub and H. M. Foley, *ibid.* 116, 914 (1959).

¹¹ H_2^+ is the simplest molecular system. Theoretical discussions of the radio-frequency spectra of H_2^+ have been given by M. J. Stephen and J. P. Aufray, J. Chem. Phys. 31, 1329 (1959); M. Mizushima, Astrophys. J. 132, 493 (1960); B. F. Burke, *ibid.* 132, 514 (1960); A. Dalgarno, T. N. L. Patterson and W. B. Somerville, Proc. Roy. Soc. (London) A259, 100 (1960); and I. H. G. Dehmelt and K. B. Jefferts, Phys. Rev. 125, 1318 (1962). However, no experimental results on this system have been reported at the time of the writing of the present paper.

¹² W. Kolos and C. C. J. Roothaan, Revs. Modern Phys. 32, 219 (1960). (Potential curve and dissociation energy of H_2).

¹³ J. P. Aufray and J. W. Cooley, Phys. Rev. 122, 1203 (1961). (Nuclear spin-spin interaction in the ground state of H_2 .)

¹⁴ G. Herzberg and A. Monfils, J. Mol. Spectroscopy 5, 482 (1960). (Measurement of dissociation energy of H_2 .) It should be pointed out that there are still some unsettled questions about the effect of nuclear motion.

¹⁵ H. G. Kolsky, T. E. Phipps, Jr., N. F. Ramsey, and H. B. Silsbee, Phys. Rev. 87, 395 (1952). (Nuclear spin-spin interaction in H_2 .) See also reference 31.

* Alfred P. Sloan Foundation Fellow. This research has been assisted by a grant from the National Science Foundation.

¹ W. Lichten, Phys. Rev. 120, 848 (1960).

² The term "fine structure" has been applied in various senses by previous authors. In this and in following papers fs will denote the splitting of a single rotational level of a molecule by interactions of the electronic spins with each other and with the other angular momenta of the molecule, exclusive of nuclear spin.

³ Free electron: A. A. Schupp, R. W. Pidd, and H. R. Crane, Phys. Rev. 121, 1 (1961); C. M. Sommerfield, *ibid.* 107, 328 (1957); Free muon: G. Chappak, F. J. M. Farley, R. L. Garwin, T. Muller, J. C. Sens, V. L. Telegdi, and A. Zichichi, Phys. Rev. Letters 6, 128 (1961).

⁴ For a summary on positronium, H, D, He⁺, and He, see H. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* (Academic Press Inc., New York, 1957). It should be pointed out that nucleon and nuclear structure effects are not yet completely understood. These affect chiefly hyperfine structure.

⁵ E. S. Dayhoff, S. Trichwasser, and W. E. Lamb, Phys. Rev. 89, 106 (1953).

⁶ C. W. Drake, V. W. Hughes, A. Lurio, and J. A. White, Phys. Rev. 112, 1627 (1958).

exact comparison of experimental results with theoretical predictions will be possible also in the case of the $c\ ^3\Pi_u$ state.

In the $c\ ^3\Pi_u$ state, para- H_2 has rotational and orbital electronic angular momenta; it is in a triplet state with two unpaired electron spins; ortho- H_2 also has two unpaired nuclear spins. The existence of all these angular momenta furnishes a greater generality of interactions than has been available previously for precise radio-frequency measurements in any molecule. Moreover, since H_2 is still a relatively simple physical system the measurement of these properties would be of great interest.

A. Electronic Structure of H_2

The spectrum of molecular hydrogen first was reported by Plücker and Hittorf¹⁶ in 1865. For almost half a century it remained an object of mystery and controversy. Because of its open, many lined structure and absence of obvious bands, it was difficult to classify as a molecular spectrum; in fact, many refused to attribute it to H_2 at all, but maintained it was due to an impurity. Eventually, it was believed to arise from hydrogen in some form, and went by the name second spectrum.¹⁷

Fulcher¹⁸ was the first to arrange some of the lines into the familiar Deslandres band scheme¹⁹ which is characteristic of a molecular spectrum. However, little progress was made in the analysis of the spectra until the decade 1924–1934. Richardson's monograph,²⁰ published at the end of this period, contains an essentially complete analysis of the spectrum and description of the electronic energy levels of H_2 .²¹ A more recent tabulation of energy levels is given by Dieke.²²

B. Fine Structure

Optical spectroscopy revealed very little about the fine structure of H_2 . The first step forward was the discovery of fs in the $b\ ^3\Pi_g$ state of the $(He)_2$ molecule by Mulliken and Monk.²³ The triplet structure was only

partially resolved into a doublet splitting. However, on the basis of visual intensity estimates, Mulliken and Monk made an assignment of the relative grouping of the levels. Shortly thereafter, Richardson and Williams²⁴ found a quite similar partially resolved splitting in the corresponding $c\ ^3\Pi_u$ level of H_2 . Extensive interferometric experiments carried out over a period of more than twenty years failed to resolve completely the fs in the $c\ ^3\Pi_u$ state or to reveal fs in any other triplet states of H_2 .²⁵

Heisenberg²⁶ had interpreted the fine structure of the $(1s,2p)\ ^3P$ state of He in terms of spin-spin, spin-orbit and spin-other-orbit interaction. Despite the fact that the $^3\Pi$ states of H_2 and $(He)_2$ are closely analogous to the 3P state of He,²⁷ no attempt was made to interpret the fs of H_2 or $(He)_2$ in terms of Heisenberg's theory. It was only after the first complete resolution of the triplet fine structure was attained by molecular beam techniques¹ that Mizushima and Frey²⁸ and Fontana²⁹ treated the problem theoretically.

It is somewhat ironic that this problem has lain neglected for more than thirty years. Despite the difficulty in interpreting the extremely incomplete data in their hands, it appears²⁹ that Mulliken and Monk²³ made an essentially correct interpretation of their measurements.

C. Molecular Beam Experiments

Almost simultaneously with the appearance of Richardson's book,²⁰ Stern and co-workers applied the technique of molecular beams to the study of the ground state of H_2 . They simultaneously measured the rotational magnetic moment of H_2 and discovered the unexpected and still unexplained anomalous proton moment.³⁰ The application of the molecular beam magnetic resonance method³¹ to the study of H_2 , HD, and D_2 by Rabi and co-workers led to the unanticipated discovery of the deuteron quadrupole moment.³²

The experimental measurements and theoretical analysis of the structure of H_2 were greatly refined by Ramsey and co-workers^{15,32} in an exhaustive series of articles, which extended over a total period of almost two decades.

The publication of Ramsey's book marked the virtual completion of the detailed study of the properties of the

¹⁶ J. Hittorf, J. W. Plücker, Phil. Trans. Roy. Soc. (London) **A155**, 1 (1865).

¹⁷ It is perhaps interesting to note that the molecular spectrum of H_2 still is listed as the "second spectrum" of atomic hydrogen in the *Handbook of Chemistry and Physics*, edited by C. D. Hodgman, (Chemical Rubber Publishing Company, Cleveland, Ohio, 1961), 43rd ed.

¹⁸ G. S. Fulcher, *Astrophys. J.* **37**, 60 (1913).

¹⁹ H. Deslandres, *J. phys.* **10**, 276 (1891).

²⁰ O. W. Richardson, *Molecular Hydrogen and its Spectrum* (Yale University Press, New Haven, Connecticut, 1934). For recent progress in the assignment of H_2 energy levels, see E. R. Davidson, *J. Chem. Phys.* **35**, 1189 (1961).

²¹ For a more complete early history of molecular spectroscopy or of the spectroscopy of H_2 in particular, see A. Kratzer, in *Encyklopädie der Mathematischen Wissenschaften* (B. G. Teubner, Leipzig, 1925), Vol. V₃, Part 5, p. 821, reference 20; W. Jevons, *Report on Band Spectra of Diatomic Molecules* (The Physical Society, London, 1932); A. Sommerfeld, *Atomic Structure and Spectral Lines*, translated from the 3rd German edition (E. P. Dutton and Company, New York, 1923), Chap. VII.

²² G. H. Dieke, *J. Mol. Spectroscopy* **2**, 494 (1958).

²³ R. S. Mulliken and G. Monk, *Phys. Rev.* **34**, 1530 (1929).

²⁴ O. W. Richardson and W. E. Williams, *Nature* **127**, 481 (1931).

²⁵ E. W. Foster and O. W. Richardson, *Proc. Roy. Soc. (London)* **A189**, 149 (1947).

²⁶ W. Heisenberg, *Z. Physik* **39**, 499 (1926) see also reference 4.

²⁷ A detailed discussion of this analogy will be given in Sec. 4B of this paper.

²⁸ M. Mizushima and D. A. Frey, *Bull. Am. Phys. Soc.* **6**, 165 (1961).

²⁹ P. R. Fontana, *Phys. Rev.* **125**, 220 (1962).

³⁰ R. Frisch and O. Stern, *Z. Physik*, **85**, 4 (1933); I. Estermann and O. Stern, *ibid.* **85**, 17 (1933).

³¹ I. I. Rabi, J. R. Zacharias, S. Millman, and P. Kusch, *Phys. Rev.* **53**, 318 (1938); **55**, 526 (1939).

³² M. B. Kellogg, I. I. Rabi, N. F. Ramsey Jr., and J. R. Zacharias, *Phys. Rev.* **55**, 318 (1939); **56**, 728 (1939).

ground state of the hydrogen molecules.³³ The diamagnetic ground state of H_2 has served as a valuable prototype for the phenomena of nuclear resonance.

Several years ago it was suggested that the lowest vibrational level of the $c^3\Pi_u$ state of H_2 is metastable.³⁴ In a recent publication¹ this was verified. Further, it was shown that electron bombardment of ortho or para H_2 led to excitation of only one observable rotational level in each case. Measurement of the linear Zeeman effect gave Landé g factors which were in excellent agreement with the assumption of case b coupling. (It will be recalled¹ that in Hund's case b , the electronic orbital and rotational angular momentum couple to form a quantized angular momentum N . For each rotational level, $(N)^2 = (N)(N+1)$ and $N=1, 2, 3 \dots$ for Π states. Furthermore, in para- H_2 , N and the electronic spin S couple to form J , the total angular momentum.)

From the quadratic Zeeman effect, a preliminary estimate was made of the fs of the $N=2$ rotational level of para- H_2 (Fig. 1):

$$f(J=2 \leftrightarrow J=3) = 5730 \pm 200 \text{ Mc/sec,}$$

$$f(J=2 \leftrightarrow J=1) = 5000 \pm 200 \text{ Mc/sec.}$$

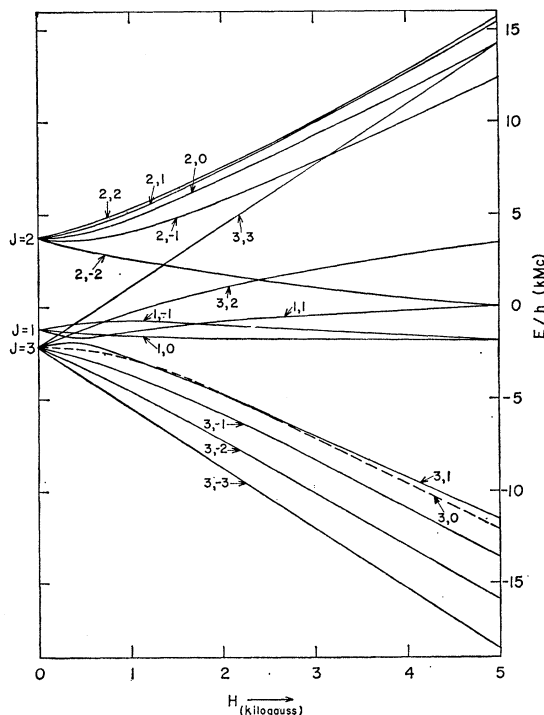


FIG. 1. Fine structure and Zeeman effect of the H_2 , $c^3\Pi_u$, $N=2$ ($v=0$), $J=3, 2, 1$ states.

³³ N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956). Since the publication of this book, two papers on the HD molecule have appeared: N. F. Ramsey and H. R. Lewis, *Phys. Rev.* **108**, 1246 (1957) and W. E. Quinn, J. M. Baker, J. T. LaFourrette, and N. F. Ramsey, *ibid.* **112**, 1929 (1958). However, the results of these papers are in complete agreement with the theoretical and experimental results from H_2 and D_2 , as described in Ramsey's book.

³⁴ W. Lichten, *J. Chem. Phys.* **26**, 306 (1957).

TABLE I. Typical experimental parameters.

Detecting circuit sensitivity: (current required to produce 1 mm galvanometer deflection)	8×10^{-17} amp
Detecting circuit input resistance	10^{12} ohms
Detecting circuit time constant	7.5 sec
Calculated rms thermal noise (in equivalent amperes at input)	0.3 mm (2×10^{-17} amp)
Observed rms noise, with H_2 beam on	0.4 mm (3×10^{-17} amp)
H_2 photon background	200 mm
H_2 : $J=3$, $\Delta m_J = \pm 1$ intensity	100 mm
He: 2^3S_1 , $\Delta m_J = \pm 1$ intensity	2000 mm
Bombarding current	5 mamp
Bombarding voltage for H_2	15 v
Bombarding current density	~ 0.5 amp/cm ²
Source pressure	~ 0.1 mm (est.)
Source chamber pressure	10^{-5} mm
Field strength in "A" and "B" magnets	3000 gauss

The possibility of a large number of experimental measurements of the Zeeman effect, fine and hyperfine structure of the $c^3\Pi_u$ state of H_2 , HD, and D_2 suggested themselves. However, a direct measurement of the fs of H_2 ($c^3\Pi_u$, $N=2$) appeared to be most interesting and feasible. Therefore, it was the first experiment to be tried. The following paragraphs give an account of the measurements.

2. APPARATUS

The apparatus has been described previously.¹ It was a molecular beam, magnetic resonance machine which was especially designed for the study of metastable molecules. (Fig. 3). Two modifications needed for the present experiment were the introduction of the microwave equipment necessary for the fine structure measurements and improvement of the signal-to-noise ratio.

The microwave measuring equipment consisted of a Gertsch FM-4A microwave frequency multiplier, driven by a carefully calibrated Gertsch FM-6 frequency meter, which was in turn driven by a very stable (drift rate 1 part in 10^{10} per day) Collins 40K-1 1-Mc/sec crystal oscillator which was compared occasionally with WWV. This system is very convenient and is accurate to one part in 10^7 .

The sources of rf power for generating the oscillating magnetic field were klystrons, stabilized by shock mounting in oil baths, and by use of a regulated power supply for the beam current and batteries for the repeller voltage. An Eitel-McCullough 1K125CB klystron was used for the 5000-Mc/sec transition and a Varian Associates VA220F klystron for the higher frequency line. Both tubes furnished more power than one watt, which was considerably more than was needed.

Because of the compact dimensions of the apparatus, difficulty was encountered in shielding the detector circuit from the hairpin. Sharp resonances were encountered which masked the H_2 spectrum. Finally, the simple expedient of placing a sealed glass tube filled with salt water near the detector greatly diminished spurious resonances at microwave frequencies.

The signal was doubled by making the channel-shaped source slit an additional part of the anode of the electron bombardment diode. This resulted in a rather large photon background. However, careful regulation of the bombardment conditions led to negligible noise, other than that arising from the thermal noise of the electrometer grid resistor. Typical experimental parameters are shown in Table I. These conditions were only fully achieved in the second half of the experiment, when the weaker $J=2 \leftrightarrow J=1$ line (see Fig. 2) was measured. Typical signal to noise ratios ranged from 5/1 to 10/1 (Fig. 2).

The shielded rf transition loop was a small parallel plane loop of the type originated by Kusch.^{35,36} However, because it had to fit into the narrow "C" magnet gap it was asymmetrical. It was designed to observe π transitions ($\Delta m_J = \pm 1$), although the asymmetry caused σ transitions ($\Delta m_J = 0$) also. Preliminary tests with a probe revealed no resonances in the region 4800–6000 Mc/sec. The transition region was 6 mm long.

3. PROCEDURE AND RESULTS

Search for the lines was facilitated by the preliminary values for the frequencies obtained from quadratic Zeeman effect studies¹ (see paragraph 1). Figure 2 shows the observed spectra of both lines. The rf amplitude was approximately optimal for the π lines. The magnetic field was measured independently by means of observations on the $\text{He } ^3\text{S}_1^{(6)}$ or $\text{H}_2^{(1)}$ low-frequency ($\Delta J=0$) lines. The theoretical spectrum was calculated using the center frequency as the only unknown parameter. Linear and quadratic Zeeman effects were calculated from theoretical values.¹

It can be seen from Fig. 2 that a complicated central structure was observed. A line of this type was first

TABLE II. Results of all runs.

Run	Lines observed	Frequency (Mc/sec)	Number of measurements	Standard error (kc/sec)
$\text{H}_2, N=2, J=3 \leftrightarrow J=2$				
1	π	5898.108	8	13
2	π	5898.106	8	9
3	σ	5898.096	4	9
4	π	5898.125	8	12
5	π	5898.089	10	6
Mean		5898.105	38	6
$f = 5898.105 \pm 0.012$ Mc/sec				
$\text{H}_2, N=2, J=2 \leftrightarrow J=1$				
1	π, σ	4927.998	5	6
2	σ	4928.012	6	9
3	π	4927.995	12	8
4	π	4928.001	8	2
5	σ	4928.009	6	6
Mean		4928.003	37	3
$f = 4928.003 \pm 0.010$ Mc/sec				

³⁵ A. K. Mann and P. Kusch, Phys. Rev. **77**, 427 (1950).

³⁶ See, for example, P. Kusch and V. W. Hughes, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 37/1, Fig. 58b.

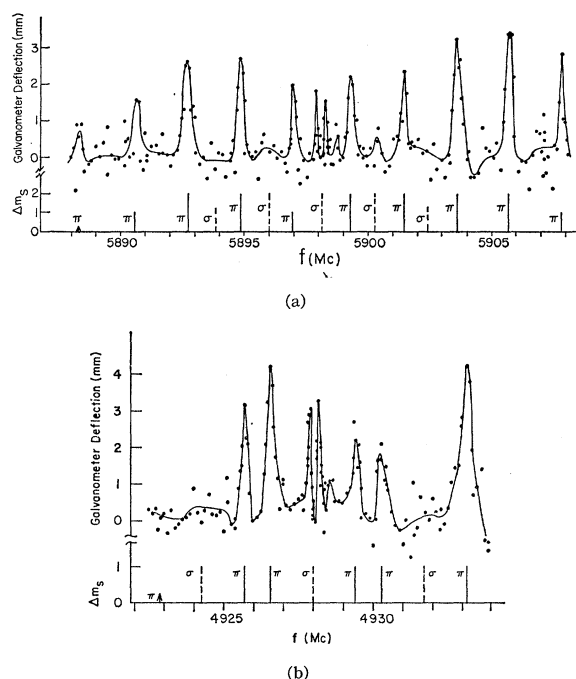


FIG. 2. Spectrum of direct transitions between fine structure levels of $\text{H}_2, c^3\Pi_u, N=2$ ($v=0$). (a) $J=3 \leftrightarrow J=2$; (b) $J=2 \leftrightarrow J=1$.

observed by Mann and Kusch.³⁵ They pointed out that asymmetries in beam traversal and excessive rf power lead to an out-of-phase Ramsey pattern³³ for a σ line ($\Delta m_J = 0, \Delta J = \pm 1$). The central minimum of such a pattern lies at the zero-field interval frequency, plus a small quadratic correction. Other workers have verified these conclusions.^{37,38}

Table II contains the results of all runs used in the computation of final results. Each set of measurements contains at least one run of each of the following types: (a) a spectrum similar to that shown in the figures, in which all observable π lines occurring in pairs were used; (b) a run in which the best symmetric pair of π lines was used; (c) a run in which only the central σ line was used. In runs of type (a), a linear Zeeman correction plus quadratic correction was applied to each line. In runs of types (b) and (c), only a quadratic correction was required. Typical quadratic corrections were of the order of 20 kc/sec. The rf power was adjusted to give optimal intensity. Power required was 100–500 mw.

In the case of the ($J=2 \leftrightarrow J=3$) lines there was no evidence of any systematic differences among runs of types (a), (b), and (c). Each run was taken to be a single observation, and the final error taken to be twice the standard error of the mean. In the case of the ($J=2 \leftrightarrow J=1$) measurement, improvements in technique caused the signal-to-noise ratios to be considerably

³⁷ G. K. Woodgate and R. W. Hellwarth, Proc. Phys. Soc. (London) **A69**, 588 (1956).

³⁸ W. J. Childs, L. S. Goodman and L. J. Kieffer, Phys. Rev. **122**, 891 (1961).

higher. The result was smaller standard errors for individual runs and the appearance of apparent systematic differences among runs. Since these differences were not investigated further, the final error was taken as three times the standard error of the mean of all runs. Since the results of all runs fall within this error, it is believed to be conservative enough to cover systematic effects.

The final results for the zero-field frequencies are:

$$f(J=2 \leftrightarrow J=1) = 4928.003 \pm 0.019 \text{ Mc/sec},$$

$$f(J=3 \leftrightarrow J=2) = 5898.105 \pm 0.012 \text{ Mc/sec}.$$

Alternatively, one can express the results in the standard form²³:

$$\frac{H}{h} = aS \cdot N + b \frac{3(S \cdot N)^2 + \frac{3}{2}(S \cdot N) - (S)(S+1)(N)(N+1)}{2S(2S-1)(N)(2N-1)}$$

$$a = -637.024 \pm 0.003 \text{ Mc/sec},$$

$$b = -3544.029 \pm 0.006 \text{ Mc/sec}.$$

It has been noted that the Hamiltonian for the fs of a molecule of para- H_2 in a magnetic field is formally identical to that for an atom.¹ In this case it is convenient to make the substitution: for N substitute I , for S substitute J . Then it can be seen that the molecular fs Hamiltonian is the same as that for the hfs of an atom with both nuclear magnetic dipole and electric quadrupole interaction. This formal identity enabled the calculation of the Zeeman effect of the molecular fs. This was done using well-known formulas on the computer "George" at Argonne National Laboratory. The results are shown in Fig. 1.

The relative level order shown in Fig. 1 was com-

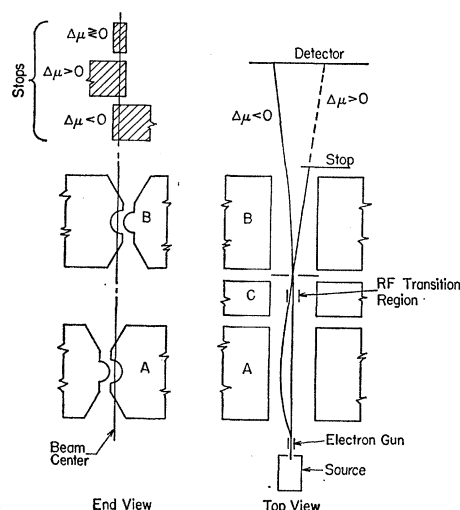


FIG. 3. Stop arrangement for determining sign of the fine structure level order. Right-hand figure shows trajectory of beam with half-plane stop inserted to select only negative moment changes. Left-hand figure shows views along the beam direction of "A" and "B" magnets and all three types of stops.

TABLE III. Results of level order experiment:
 $J=2 \leftrightarrow J=1$, $m_J=0$, $\Delta m_J=0$.

Stop	Moment change	Refocusing trajectory	Galvanometer deflection ^a (mm)	Deduced transition
			Defocusing trajectory in "A" region	
Wire	\pm	3.6	1.45	$J=2 \leftrightarrow J=1$
Half-plane	$+$	2.6	0.2	$J=2 \rightarrow J=1$
Half-plane	$-$	1.1	1.1	$J=2 \leftarrow J=1$

^a Mean of several observations.

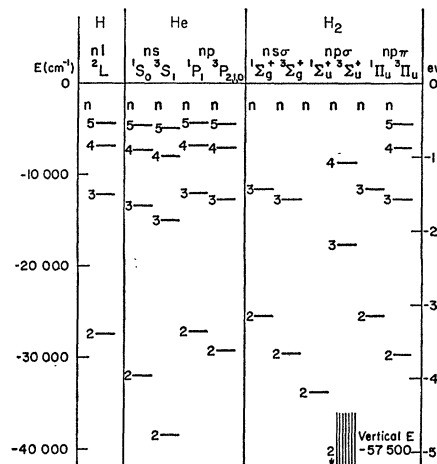
pletely determined by the Zeeman effect studies described in reference 1. The intensity patterns in Fig. 2 furnish a confirmation. However, an identical level order with a complete inversion of all the levels (change of sign of both interaction constants) is compatible with all the observations described so far. The sign of the order level had been assumed on the basis of the partially resolved optical data.¹

An experiment was performed to establish the sign on firmer grounds. The σ transitions ($J=2$, $m_J=0 \leftrightarrow J=1$, $m_J=0$) were used. It can be seen from Fig. 1 that the state ($J=2$, $m_J=0$) has a large effective magnetic moment at high fields. On the other hand, the ($J=1$, $m_J=0$) level has a very small effective magnetic moment at all fields. With the stop wire, both transitions between levels were observed. A half-plane stop allowed observation of transitions to the state of higher effective moment (Fig. 3). The other half-plane stop allowed observation only of transitions to lower effective magnetic moment. The intensities of the three types of transitions are shown in Table III. In a second experiment, the field in the "A" magnet was tripled. This had little effect on the $J=1$ molecules, since they had little magnetic moment. On the other hand, the $J=2$ molecules were defocused by the excessive field in the "A" magnet and could not reach the detector. In the second experiment only molecules undergoing the transition ($J=1 \rightarrow J=2$) produced an observable effect. This transition was observable only with the stop plane in the position corresponding to a *decrease* in effective magnetic moment, i.e., increase in energy (Table III). Thus, the results of the second experiment confirmed the previously assumed level order.^{1,25}

4. DISCUSSION OF RESULTS

The agreement between experimental line patterns (Fig. 2) and theory is excellent. The intensities also are in qualitative agreement with expectation. π lines with a high-field spin change $\Delta m_S = \pm 2$ are strong; lines with $\Delta m_S = \pm 1$ are weak, but always observable; lines with $\Delta m_S = 0$ have a very low signal to noise and are of questionable observability. (In the case of the σ lines, the rf amplitude was sufficient only to bring out with certainty the central line.)

The agreement between theory and the experimental



Hydrogen orbital	Old molecular orbital designation	New molecular orbital designation	Molecular state	Analogous helium state (united atom state)
$2s$	$2s\sigma$	$2\sigma_g$	${}^3\Sigma_g^+, {}^1\Sigma_g^+$	$2\ ^1S, 2\ ^1S$
$2p, m=0$	$2p\sigma$	$1\sigma_u$	${}^3\Sigma_u^+, {}^1\Sigma_u^+$	$2\ ^3P, 2\ ^1P$
Degenerate				
$2p, m=+1$	$2p\pi$	$1\pi_u$	${}^3\Pi_u, {}^1\Pi_u$	$2\ ^3P, 2\ ^1P$
$2p, m=-1$	$2p\bar{\pi}$	$1\bar{\pi}_u$	${}^3\Pi_u, {}^1\Pi_u$	$2\ ^3P, 2\ ^1P$

⁴¹ J. K. L. McDonald, Proc. Roy. Soc. (London) **A136**, 528 (1932). See also S. Huzinaga, Prog. Theoret. Phys. (Kyoto) **17**, 162 (1957); I. Tamásy-Lentei, Acta Phys. Acad. Sci. Hung. **12**, 119 (1960).

TABLE V. Spin-orbit and spin-spin coupling constants in He and H₂. Comparison between experimental results and hydrogenic model.

	Spin-orbit coupling constant <i>a</i>	Spin-spin coupling constant <i>b</i>
He	$(-\alpha^2/96)$ (atomic units)	$(\alpha^2/60)$ a.u.
Theory ^a	-3.65×10^3 Mc/sec	5.84×10^3 Mc/sec
Experiment ^b	-5.89×10^3 Mc/sec	6.33×10^3 Mc/sec
H ₂	$-\alpha^2/[96(N)(N+1)]$ a.u.	$\frac{\alpha^2}{24} \left\{ \frac{1}{5} \left[\frac{3}{(N)(N+1)} - 1 \right] \pm \frac{3}{5} \right\} \frac{N}{2N+3} = -\frac{\alpha^2}{120}$ a.u.
Theory ^c	-608 Mc/sec	-2.92×10^3 Mc/sec
Experiment ^d	-637 Mc/sec	-3.54×10^3 Mc/sec

^a Calculated from data given in reference 4. The theoretical expression for the fs of He is the same as that for H₂ (Sec. 3, present paper), except that *L* should be substituted for *N*.

^b See reference 10.

^c Calculated from information given in reference 29.

^d See Sec. 3, present paper.

becomes indistinguishable from a He (*n*=2) electron. Thus, the H₂⁺ states listed in Table IV are analogs of the corresponding He states.

For the outer electron, this analogy holds rather well, even when the nuclei are separated by distances typical of H₂.⁴⁰ Strictly speaking, the fs is a property of both electrons. Nevertheless, it will be shown in the following paragraph that the fs is rather independent of the properties of the inner electron and is approximately dependent on a quasi-one electron operator involving

the coordinates of the outer electron. Thus, the fs of H₂⁺ is quite similar to that of He, 2³P.

On the other hand, the hyperfine structure (hfs) arises largely from interactions of electrons in contact with, or close to the nuclei. Thus, for H₂⁺, the outer electron plays a subsidiary role and the core determines the hfs. The hfs is not at all similar to that of He, but is close to that of H₂⁺. It is planned to discuss hfs in a later article.

B. The *c*(1σ_g,1π_u) ³Π_u State of H₂

The application of the McDonald model to the specific state of interest, *c* ³Π_u, is illustrated in Fig. 5. It can be seen from examination of Fig. 5 that the spatial extent of the inner electronic wave function is small compared to that of the outer electron for both He and H₂. This lends plausibility to the assumption of a simplified hydrogenic model for He, in which the inner electronic wave function is assumed to be concentrated at the origin. The outer electron is assumed to be in an atomic hydrogen 2*p* orbital. It is reasonable to assume an analogous united atom model for H₂, in which both nuclei and the inner electron are concentrated at the origin. This is seen to be a simplified version of the McDonald model.

Table V compares theoretical and experimental results for both He and H₂. To bring out the physical significance of the results, the standard constants *a* and *b* have been given. It has been shown that *a* arises only from spin-orbit and spin-other-orbit interaction; *b* arises only from spin-spin interaction.^{4,29}

It is interesting to note that there is reasonably good agreement between the predictions of the simplified hydrogenic model and experimental results, except in the case of the spin-orbit coupling constant, *a*, for He. This difference may be related to the fact that the effective *Z* for He becomes 2 near the nucleus, whereas it remains 1 for H₂. Also it may be noted (Fig. 5) that the outer electron actually penetrates the inner orbital less for H₂ than for He. Thus, shielding is perhaps more complete. Nevertheless it is surprising that coupling constants of the molecular system are in better agree-

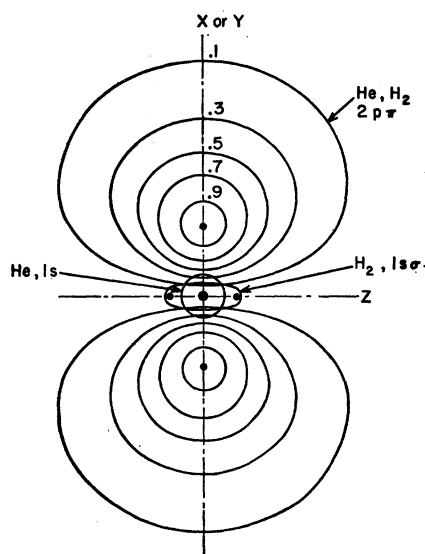


FIG. 5. Wave functions for He and H₂. Contours shown are for equal relative probability density, the maximum value being equal to unity. The figures represent a cross-section through the *Z* axis (internuclear axis of H₂).

The wave functions shown for He and for nonrotating H₂ have cylindrical symmetry. In the rotating molecule the *p*π orbitals no longer are symmetric about the *Z* axis, but break up into non-degenerate π⁺ and π⁻ orbitals, each of which is rotationally symmetric about the *x* and *y* axis. The outer electron wave function is taken to be a hydrogen 2*p* orbital with *Z*_{eff}=1. The inner electron orbitals are taken to be the same as He (1*s*, *Z*_{eff}=2) and H₂⁺ wave functions. Only the contours with relative probabilities of 1.0 and 0.1 are shown for the inner electrons. The positions of maximum probability for the inner wavefunctions are at the nuclei of He or H₂.

TABLE VI. Fine structure effects in H_2 .

Interaction or error	Order of magnitude (Mc/sec)	Relative size
(A) Spin-orbit, spin-other-orbit, and spin-spin coupling ^{a,b}	5000	1.0
(B) Change in fs per vibrational quantum ^c	200	5×10^{-2}
(C) Spin-rotation interaction, rotational distortion and other nuclear motion effects ^d	10	2×10^{-3}
(D) Higher order quantum electrodynamic corrections (largely effect of the anomalous electron magnetic moment) ^e	10	2×10^{-3}
(E) Breakdown of case <i>b</i> coupling by perturbation of rotational fs by magnetic fs ^f	5	1×10^{-3}
(F) Uncertainty in theoretical fs due to errors in fine structure constant, ^g	0.1	2×10^{-5}
(G) Error in present measurement ^h	0.01	2×10^{-6}

^a Reference 29.^b Present paper^c Reference 25.^d M. H. Hebb, Phys. Rev. **49**, 610 (1936).^e G. Araki, Phys. Rev. **101**, 1410 (1956).^f E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928), also P. Fontana (private communication). Second order interactions involving other electronic states are much smaller than those involving nearby rotational levels.^g Reference 5. See also Table V.

ment with the simplified hydrogenic model than those of the He atom.

C. Finer Effects

It is of interest to speculate how precisely one can compare the present experimental results with theoretical calculations. The considerations necessary for a discussion of such a comparison are listed in Table VI. Since electromagnetic interactions appear to be very well understood⁴² and other interactions play a negligible role in molecules such as H_2 , the ultimate limitations are the accuracies of the experimental measurement [Table V (G)] and of the natural constants. It appears that such a comparison would be limited chiefly by the factor α^2 , which has been measured to an error⁵ of 2 parts in 10^5 [Table VI (F)].

However, in the case of the two-electron system of H_2 , only approximate wave functions are available. One limitation is that the solutions to Schrödinger's equation are obtained by variational calculations. In the case of the ground state of H_2 , the wave function of

Kolos and Roothaan appears to yield an energy accurate to a few parts in 10^6 , and other molecular interactions¹³ to a few parts in 10^3 . The $c\ ^3\Pi_u$ state is the lowest state of its symmetry type. Moreover, it is a triplet state, which appears to simplify variational calculations.⁴³ Therefore, there seems to be no reason why a comparable accuracy could not be achieved for a wave function for the $c\ ^3\Pi_u$ state.

A second limitation of molecular calculations lies in the assumption of the Born-Oppenheimer approximation.⁴⁴ The chief effect of this approximation is to neglect the coupling of the electronic wave functions to nuclear motions [Table VI (C)]. In addition, there are other small effects of the order of a few parts in 10^3 , which depend on higher order quantum electrodynamic corrections [Table VI (D)] and other perturbations [Table VI (E)].

The cumulative limitation of these effects appears to be that a rigorous test of the theory of molecular fine structure can be made to a precision of a few tenths of a per cent. Smaller effects could be measured experimentally by observing the variation of interaction constants with rotational quantum number, or by comparing fs of different isotopic molecules. Theoretical investigations could be made by means of perturbation theory.⁴⁵ Thus, there is some hope that these finer details also can be investigated to some extent, despite the limitations of present-day molecular theory.⁴⁶

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⁴³ See, for example, reference 9.⁴⁴ M. Born and J. R. Oppenheimer, Ann. Physik, **84**, 457 (1927).⁴⁵ For example, see Table VI, references *d* and *f*.⁴⁶ The one-electron H_2^+ system can be treated exactly within the Born-Oppenheimer approximation: variational calculations are not needed. Nevertheless, the same small effects [Table VI (C, D, E)] are present in H_2^+ , as in H_2 . Thus the precision of interpretation of the proposed H_2^+ experiments (reference 11) is about the same as for the present case.⁴² See references 3-9.