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Metastable Hydrogen Molecules

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The existence of a metastable electronic state of H_2 has been established by means of the molecular beam magnetic resonance technique. Observations have been made of the radio-frequency Zeeman spectrum of natural and para-hydrogen. At a magnetic field of about 5 gauss the strongest line corresponds to a g value of 0.83. The appearance potential for this line is 11.9 ± 0.25 ev. Observation of the quadratic Zeeman effect made it possible to estimate the fine structure of the $N=2$ level of para-hydrogen. The observed intervals are: $f(J=2\leftrightarrow J=3)=5730\pm200$ Mc/sec, $f(J=2\leftrightarrow J=1)=5000\pm200$ Mc/sec. This represents the first complete resolution of the fine structure of a rotational level of H_2. Knowledge of the electronic structure of H_2, agreement of the appearance potential with spectroscopic data, agreement of the fine structure with partially resolved optical spectra, and good agreement of the Zeeman spectra with theory lead to the conclusion that the metastable state must be H_2, $c(1\sigma_g, 1\pi_u)\,{}^3\Pi_u$.

INTRODUCTION

A FEW years ago, the author found some experimental evidence to support the hypothesis that the $c\,{}^3\Pi_u$ $(v=0)$ state of H_2 is metastable.[1] Bombardment of H_2 molecules by electrons of controlled energy led to an observable current in a secondary electron emission detector. The appearance potential (11.9 ev) was in good agreement with the spectroscopic value ($V_{00}=11.86$ ev). Nevertheless, the experiment was not conclusive since it was not proven that photons could be excluded as a cause for the observed signal.

Recently, the Rabi (atomic beam magnetic resonance) technique has been used to identify metastable states produced by electron bombardment of atoms.[2] The present paper describes the use of these methods to verify that metastable molecular H_2 does exist.

METHOD

A molecular beam apparatus, specifically designed for the study of metastable molecules has been built at Ryerson Laboratory, University of Chicago (Fig. 1). The distance from source to stop wire was made small (12 cm) in order to achieve good beam intensity. To accomplish compactness it was necessary to make the A, B, and C magnets small and close to each other. To avoid fringing of the A and B fields into the C region, the gap in the C magnet was only 3.2 mm. The ratio of gradient to field in the A and B magnets was 6 cm^{-1}, corresponding to a beam height of approximately 3 mm.

After emerging from the source, the molecules were bombarded by a narrow (0.08 mm) electron beam in order to produce metastables. The electron beam was collimated by a uniform magnetic field (about 1600 gauss) produced by a small permanent magnet. To overcome recoil dilution (loss of beam collimation by electron recoil after impact), it was found necessary to make the separation of the source and electron gun anode less than 1 mm.

The flop-out geometry (Fig. 1) was identical with that used in the atomic experiments.[2] This insured that all transitions with a large change in high-field magnetic moment corresponded to observable changes in trajectory.

A nickel secondary electron emission detector with a conventional electrometer amplifier was used. Sensitivity was one mm deflection for 5×10^{-16} amp.

PROCEDURE AND RESULTS

Resonances were found in the metastable detector current as a function of frequency for H_2 molecules [Fig. 2(a)]. The magnetic field was calibrated by observing the Zeeman transitions in metastable He, ${}^3S_1$ $(\Delta m_J=\pm1)$. The frequency of these transitions is given by the relation, $hf=g_J\mu_0H$, where $g_J(\text{He}, {}^3S_1)$

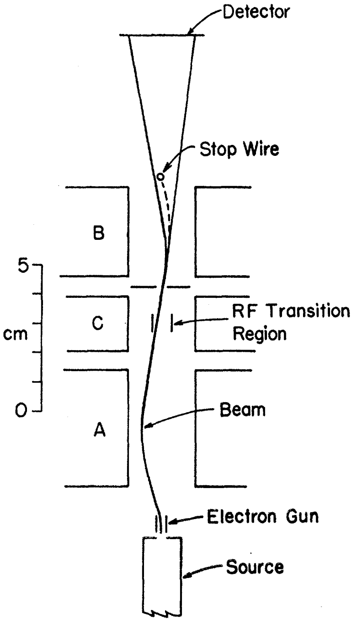

FIG. 1. Apparatus: The metastable molecules are refocussed on to the stop wire (broken line). In case of an rf transition leading to a change in moment, molecules follow a trajectory (solid line) that misses the stop wire and strikes the detector. Horizontal dimensions are not drawn to scale.

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[1] W. Lichten, J. Chem. Phys. **26**, 306 (1957).

[2] M. McDermott and W. Lichten, Phys. Rev. **119**, 134 (1960).

$= 2.002232 \pm 0.000020$.[3] The most striking feature of the H_2 results at low magnetic fields (≈ 5 gauss) is a strong line corresponding to a g factor of approximately 0.83. The electron energy was calibrated by means of the known appearance potential for He, $^3S_1$, 19.8 ev.[4] An excitation function for the strong H_2 transition was obtained (Fig. 3). The threshold for excitation was 11.9 ± 0.25 ev.

Para-hydrogen was obtained by placing a small amount of catalyst[5] in the bottom of a small glass Dewar and filling it with liquid H_2. After a few hours, the liquid was largely converted to para-H_2. The evaporating para-H_2 was passed into the source of the apparatus. The Zeeman spectrum was simpler than that of natural H_2. Essentially only two lines were observed at $g = 0.78$ and $g = 0.47$ [Fig. 2(b)].

Because of overlapping of lines and field inhomogeneities the low-frequency lines were broad (500–800 kc/sec) and g values were inaccurate. In an attempt to obtain more accurate g values and to resolve blended lines, measurements were made at fields as high as 100 gauss. At about 20 gauss, the strong line for natural H_2 was observed to split into two lines with g values of 0.78 and 0.83, respectively. On the other hand, at comparable fields, the $g = 0.78$ line for para-H_2 was single. In the case of the weaker lines present in the natural H_2 spectrum, the signal to noise ratio was less favorable, and no attempt was made to observe these lines at higher fields.

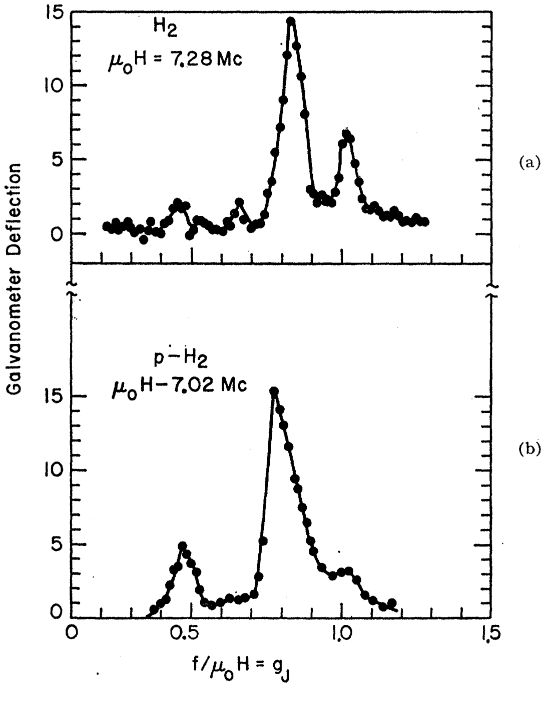

FIG. 2. Low-frequency Zeeman transitions: (a) Upper figure: natural H_2 (75% ortho-H_2, 25% para-H_2). (b) Lower figure: para-H_2.

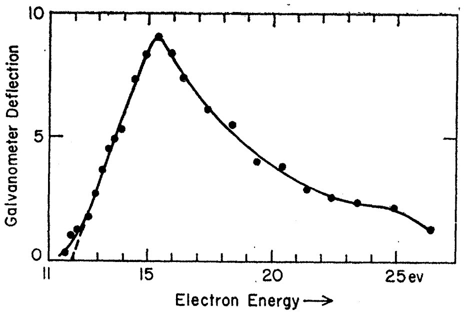

FIG. 3. Excitation function for the line $g = 0.83$ of natural H_2.

At the highest magnetic fields the $g = 0.47$ line remained single, whereas the $g = 0.78$ line split into two components of approximately equal intensity. The linewidths narrowed to approximately 300 kc/sec. This is equal to the theoretical broadening due to the uncertainty principle. The sharpening of the lines made possible relatively accurate measurement of the linear and quadratic terms of the Zeeman effect for these three lines. Final results for the linear Zeeman effect are presented in Table I. Results for the quadratic effect are discussed in the next section.

DISCUSSION

1. Metastable H_2

The presence of radio-frequency resonances in the detector signal proves the presence of metastable molecules. The appearance potential (11.9 ± 0.25 ev) is in excellent agreement with previous results[1] and the spectroscopic value for the lowest vibrational level for H_2, $c\ ^3\Pi_u$. Figure 4 shows the energy levels for the lowest excited states of H_2. The vibrational levels are taken directly from experimental term values given by Dieke.[6] Potential energy curves are Morse curves calculated from experimental constants,[7] or are taken from more elaborate treatments of experimental data[8] or from the best available theoretical calculations.[9]

Examination of the term scheme for H_2 and of selection rules for diatomic molecules shows that no known state, except $c\ ^3\Pi_u$, can be metastable. The lowest excited state, $b\ ^3\Sigma_u^+$, is repulsive and dissociates in $\approx 10^{-14}$

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[3] C. W. Drake, V. W. Hughes, A. Lurio, and J. A. White, Phys. Rev. **112**, 1627 (1958). Note: apparently there is a misprint in the error given in this article. The authors give an alternative semi-theoretical value, $g_J = 2.002237$. The difference between these values is insignificant for purposes of the present experiment.

[4] It was necessary to perform this experiment with a mixture of H_2 and He. Otherwise, erroneous results arose from a change in the work function of the tungsten filament when gases were changed.

[5] Harshaw chrome alumina tablets CR-0205T.

[6] G. H. Dieke, J. Mol. Spectroscopy **2**, 494 (1958).

[7] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Princeton, New Jersey, 1950).

[8] A. S. Coolidge and H. M. James, J. Chem. Phys. **6**, 730 (1938); A. S. Coolidge, H. M. James, and E. L. Vernon, Phys. Rev. **54**, 726 (1938).

[9] W. Kołos and C. C. J. Roothaan, Revs. Modern Phys. **32**, 205 (1960).

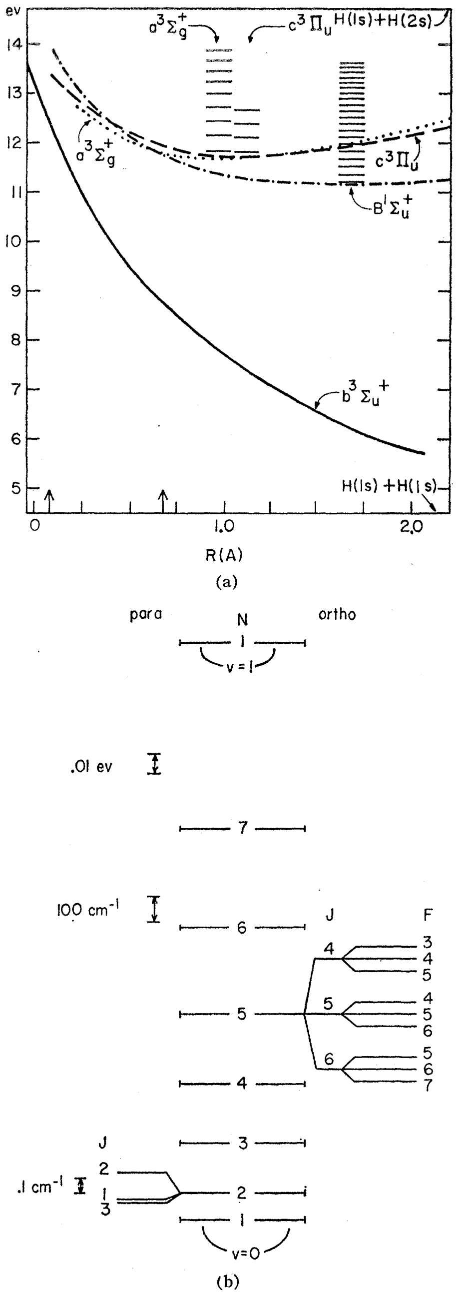

FIG. 4. Energy levels for H_2. (a) Upper figure: Energy is measured from the ground state. Potential energy curves and vibrational levels are shown. Rotational and spin fine structure are too fine to be shown on this scale. Arrows show classical turning points of ground state. The correct scale for $R(A)$ runs from 0.6 to $1.4A$, not 0 to $2A$. Sources for potential energy curves: $b\,{}^3\Sigma_u^+$, reference 8; $c\,{}^3\Pi_u$, reference 7; $B\,{}^1\Sigma_u^+$, reference 9; $a\,{}^3\Sigma_g^+$, reference 8. (b) Lower figure: energy level diagram for $c\,{}^3\Pi_u$ state of H_2, showing rotational fine structure of $v=0$ level. Lowest rotational level of $v=1$ is at extreme top of figure. Each rotational level of para-H_2 is split into three fine structure levels. Splitting for the $N=2$ level is shown on a greatly magnified scale. Each rotational level of ortho-H_2 is split into three fs levels; each fs level (with the exception of $N=1$, $J=0$) is split into three hyperfine levels. The fs and hfs of the $N=5$ level are shown diagrammatically, on a greatly enlarged scale. (Actual intervals of this level are not known.)

sec into two ground-state H atoms. $B\,{}^1\Sigma_u^+$ decays via an allowed transition with a lifetime[10] of 6×10^{-10} sec to the ground state, $X\,{}^1\Sigma_g^+$. The $a\,{}^3\Sigma_g^+$ state decays by an allowed transition to the repulsive triplet state in $\approx10^{-8}$ sec.[11] It can be shown that all other states of H_2 decay via allowed transitions to the ground state of H_2 or to repulsive states leading to separated atoms. Excitation of some states can produce H atoms in the metastable $2S$ state.[12] However, these atoms would be

TABLE I. Calculated and observed g values for H_2, $c\,{}^3\Pi_u$. (The anomalous electron moment and the g factor of the proton have been used in calculating g values. However, no higher order electrodynamic corrections or relativistic factors have been included.)

N	J	g_J(para)	F	g_F(ortho)	Observed g
1	0	...	1	−0.00304	
	1	1.25115			
			0	...	
			1	0.62405	0.66 ±0.02
			2	0.62405	
	2	1.25115			
			1	1.87824	
			2	1.04211	1.02 ±0.02
			3	0.83309	0.8338±0.003
2	1	−0.75115			
			0	...	
			1	−0.37709	
			2	−0.37709	
	2	0.47261			0.4734±0.0015
			1	0.71043	
			2	0.39333	
			3	0.31407	
	3	0.77854			0.7794±0.001
			2	1.03906	
			3	0.71341	
			4	0.58315	
3	2	−0.55633			
			1	−0.83298	
			2	−0.46411	
			3	−0.37190	
	3	0.24325			
			2	0.32534	
			3	0.22273	
			4	0.18168	
	4	0.56307			
			3	0.70460	
			4	0.53477	
			5	0.44984	
4	3	−0.43807			
			2	−0.58308	
			3	−0.40181	
			4	−0.32929	
	4	0.14762			
			3	0.18529	
			4	0.14009	
			5	0.11749	
	5	0.44046			
			4	0.52916	
			5	0.42568	
			6	0.36654	

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[10] S. Ehrenson and P. Phillipson (unpublished).

[11] H. M. James and A. S. Coolidge, Phys. Rev. **55**, 184 (1939).

[12] W. Lamb and R. C. Retherford, Phys. Rev. **79**, 549 (1950); **81**, 222 (1951). See also W. Lichten and S. Schultz, Phys. Rev. **116**, 1132 (1960).

quenched by the magnetic fields in the apparatus and would never reach the detector.

The lowest vibrational level ($v=0$) of the $c\,^3\Pi_u$ state can decay only to $b\,^3\Sigma_u^+$ via a forbidden magnetic dipole transition. The lifetime for a transition of this type should be of the order of a millisecond. At room temperature the thermal velocity of H_2 is $\approx 2\times 10^5$ cm/sec. Thus it can be seen that the decay length should be of the order of meters, and $c\,^3\Pi_u$ ($v=0$) should be effectively metastable.

On the other hand, higher vibrational levels ($v\geqq 1$) of $c\,^3\Pi_u$ can decay to $a\,^3\Sigma_g^+$. Thus it is unlikely that these levels are metastable. However, because of the low frequency of the transition $(a\,^3\Sigma_g^+ \leftarrow c\,^3\Pi_u)_{01}$, it is possible that a few molecules in the $v=1$ level reach the detector. At present, there is no experimental basis for deciding this question.

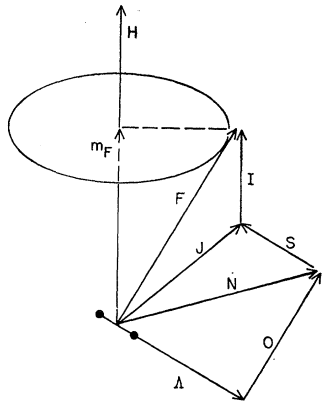

FIG. 5. Angular momenta in case *b* coupling for a diatomic molecule.

2. Zeeman Effect

In order to interpret the observed spectra, it is necessary to discuss the theory of the Zeeman effect of diatomic molecules (Fig. 5). The relative magnitudes of the various interactions are such that H_2, $c\,^3\Pi_u$ should follow Hund's case *b* coupling quite closely. In case *b* (Fig. 5), the projection of the electron orbital angular momentum along the internuclear axis, Λ, is a well-defined quantum number. For a Π state, $\Lambda=1$. The rotational angular momenta, $\mathbf{O}$, and $\mathbf{\Lambda}$, couple vectorially to form the total orbital angular momentum $\mathbf{N}$. In general, $N=\Lambda, \Lambda+1, \cdots$. Here, $N=1, 2, 3, \cdots$. The electron spin, $\mathbf{S}$, and $\mathbf{N}$ add vectorially to form the total angular momentum exclusive of nuclear spin, $\mathbf{J}$. In general, $J=N-S, N-S+1, \cdots N+S$. Since $S=1$, for a triplet state, $J=N, N\pm 1$. For para-H_2, J is the total angular momentum of the system. For ortho-H_2, the nuclear spin, $I=1$, and J couple to form the total angular momentum, $F=J, J\pm 1$.

Λ is a good quantum number as long as the rotational interaction does not mix $^3\Pi_u$ with neighboring $^3\Sigma_u$ states.[13] N is a good quantum number as long as the spin interaction does not perturb the rotational fine structure (fs). These conditions are very well obeyed since, for $c\,^3\Pi_u$, the spin fs≈ 0.2 cm^{-1}, the rotational fs$\approx 10^2$ cm^{-1}, and the nearest $^3\Sigma_u$ state is separated from $^3\Pi_u$ by $\approx 10^4$ cm^{-1} (Fig. 4).[14]

J is well defined for para-H_2 as long as the Zeeman effect does not mix states within a spin multiplet, or with neighboring rotational levels. The latter interaction was negligible at fields employed in this study; the former leads to a quadratic Zeeman effect and must be taken into account.

Thus for para-H_2 the quantum numbers Λ, N, and J should be well defined. The expression for the Zeeman effect of the fs can be derived readily in complete analogy to the atomic case, except that N must replace L in the well-known expressions[7,15,16]:

$$E(N,S,J,m)=E(J)+m_J g_J \mu_0 H+\frac{\langle N,S,J+1,m|H'|N,S,J,m\rangle^2}{E(J)-E(J+1)}+\frac{\langle N,S,J,m|H'|N,S,J-1,m\rangle^2}{E(J)-E(J-1)},$$

where m_J is the projection of J along H, μ_0 is the Bohr magneton, H the magnetic field in gauss, and

$$g_J=\frac{1}{J(J+1)}\left[\frac{J(J+1)+N(N+1)-S(S+1)}{2}g_N+\frac{J(J+1)+S(S+1)-N(N+1)}{2}g_S\right],$$

$$g_N=\Lambda^2/N(N+1),$$

$$g_S=2(1+\alpha/2\pi+\cdots)=2.0023,$$

$$\langle N,S,J,m|H'|N,S,J-1,m\rangle^2=\frac{(J-N+S)(J+N-S)(J+N+S+1)(N+S+1-J)(J^2-m^2)(g_S-g_N)^2}{4J^2(2J-1)(2J+1)}.$$

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[13] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

[14] See reference 7. Spin-orbit interaction can mix $^3\Pi_u$ with $^{1,3}\Sigma_u$ states also. In the case of H_2 this effect is quite negligible. See J. H. Van Vleck, Phys. Rev. **40**, 544 (1932); M. H. Hebb, Phys. Rev. **49**, 610 (1936).

[15] See, for example, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953), Chap. XVI. See also L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958), pp. 476–482.

[16] See S. H. Koenig, A. G. Prodell, and P. Kusch, Phys. Rev. **88**, 191 (1952) for g_S. For g_I, see N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956).

For ortho-H_2, the hfs is probably comparable to the atomic hfs (0.05 cm^{-1}). Since this is not negligible compared to the fs, one would expect some perturbation of the fs by the hf interaction. Thus, J would no longer be a good quantum number, and there is no simple expression for the Zeeman effect of the hfs. Nevertheless, the theoretical expressions for the Zeeman effect should hold approximately. In the case of the single level $F=J+1=N+2$, there is no perturbation, J is a good quantum number, and the theoretical expression for the linear Zeeman effect should be quite reliable. The expression for the linear effect is readily derived by the vector model and is the same as that in the atomic case[15,16]:

$$E(F,m_F)=E(F)+g_F\mu_0H,$$

$$g_F=\frac{1}{F(F+1)}\left[\frac{F(F+1)+J(J+1)-I(I+1)}{2}g_I+\frac{F(F+1)+I(I+1)-J(J+1)}{2}g_J\right],$$

$$g_I=-0.003\,042.$$

The theoretical g factors are compared with experimental results in Table I. It can be seen that there is good agreement with the assumption that all the observable intensity arises from excitation of only the $N=1$ level for ortho-H_2 and the $N=2$ level for para-H_2.

In particular, for the levels ($N=1, J=2, F=3$; $N=2, J=2$; $N=2, J=3$) for which the theoretical predictions are unambiguous, the discrepancies between observation and theory are within the experimental error. Thus, Hund's case b is an excellent description of these rotational levels of the $c\,^3\Pi_u$ state.

3. Fine Structure

In the case of the $N=2$ levels of para-H_2 it was possible to estimate the fs by observation of the quadratic Zeeman effect. A qualitative picture of the fs with the Zeeman effect is shown in Fig. 6. The calculated intervals are:

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

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

With the exception of a complete inversion of the levels shown in Fig. 6, no other ordering of the fs levels is compatible with the experimental data. The fine structure of the $N=2$ level of $c\,^3\Pi_u$, $v'=0$ has been partially resolved optically by Foster and Richardson.[17] On the basis of intensity measurements, the upper state was assigned to $J=2$. The center of gravity of the unresolved $J=1$ and $J=3$ levels was measured to be (0.178±0.002) cm^{-1} below the $J=2$ level. The weighted average of the present measurements is (0.184±0.006) cm^{-1}, in agreement with optical measurements. If one accepts the assignment of the optical measurements, the ordering of the fs structure is unique.

4. Intensity

A reasonable interpretation of the intensity of the para-H_2 lines can be made on the basis of the fs of the $N=2$ level (Fig. 6). Although the rf transitions occur at low field, no observable effect will result unless the deflection of the metastable molecules in the high-field A and B regions is changed (Fig. 1). This requires a large change in the high-field magnetic moment $-\partial E/\partial H$. Therefore the high-field selection rule is $\Delta m_S=\pm 1$; this is to be coupled with the low-field selection rule $\Delta J=0$, $\Delta m_J=\pm 1$. The predicted transitions are shown in Fig. 6. It can be seen that the $J=1$ transitions are unobservable and that the $J=3$ transitions should be about twice as intense as the $J=2$ line. Also, the $J=2$ line should be single and the $J=3$ line should be double at high enough magnetic fields. All these predictions, plus the ratio of the quadratic Zeeman effect for the two $J=3$ lines are in agreement with experiment.

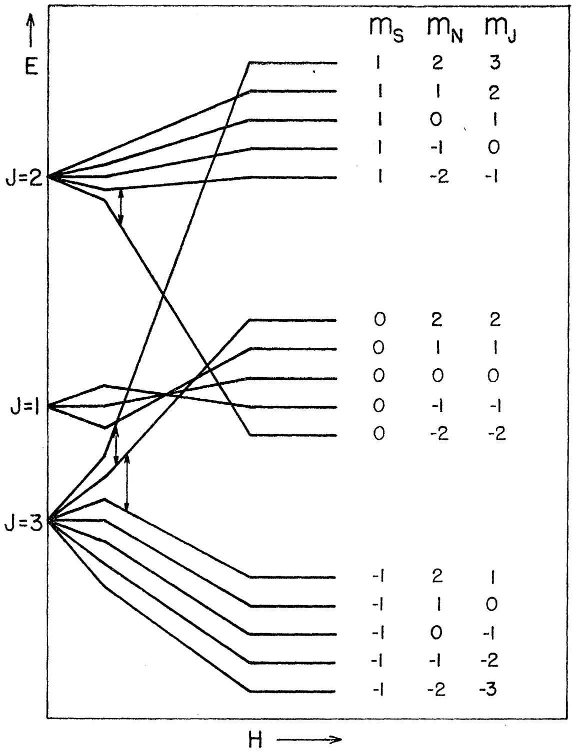

FIG. 6. Energy levels for para-H_2, $c\,^3\Pi_u$, $N=2$.

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[17] E. W. Foster and O. Richardson, Proc. Roy. Soc. (London) **A217**, 433 (1953).

It is not possible to make an unambiguous prediction about the ortho-H_2 line intensities. However, the observed intensities seem to be qualitatively in agreement with the assignment given in Table I.

Since the theory of the intensity rules for population of rotational levels of states excited by electron impact is not known, it is not possible to compare experimental results with theory. The weakness of all lines, except those arising from one ortho-H_2 and one para-H_2 rotational level appears puzzling. It is conceivable that accidental quenching of some rotational levels occurs at some particular magnetic field. However, no evidence was found for such quenching above 1600 gauss, despite a careful search. Because of the permanent magnet used for collimation of the electron beam, it was not possible to search below 1600 gauss for accidental quenching.

The determination of the fine structure by means of the quadratic Zeeman effect furnishes the first complete resolution of the spin fs of a rotational level of the H_2 molecule. The $c\,{}^3\Pi_u$ electronic state has the electronic configuration $(1\sigma_g,1\pi_u)$ in present-day molecular orbital notation.[18] In the older notation, the configuration is $(1s\sigma,2p\pi)$, which is the molecular analogue of the excited $(1s,2p)^3P$ state of atomic He. It is particularly interesting to note that precise measurements of the fs of He have been made recently by Lamb and Franken and co-workers.[19] In the light of these measurements, it seems desirable to make the H_2 measurements to a comparable precision by observing directly the transitions H_2, $c\,{}^3\Pi_u$, $N=2$, $\Delta J=\pm 1$, $\Delta m_J=0, \pm 1$.

Also, more accurate measurements of the g values would be of interest. Such measurements would involve a considerable improvement of experimental technique, plus a detailed calculation of relativistic and diamagnetic effects, plus a consideration of deviations from ideal case b coupling.

In addition, no measurements of the hfs have been made here. It would be of considerable interest to compare results for H_2 with isotopic molecules.

CONCLUSIONS

Despite the incompleteness of the present measurements and the many questions which remain unanswered, certain conclusions can be regarded as established. It is certain that metastable H_2 molecules can exist. There is little doubt that the lowest one or two vibrational levels of $c\,{}^3\Pi_u$ are the metastable states. In addition, measurements of the Zeeman effect have confirmed that the case b coupling rules are very well obeyed. Preliminary measurements have been made of the fs of the $N=2$ rotational level of para-H_2. The internal coherence of all these measurements and external agreement with theory and other experimental measurements constitutes a basis for further experiments.

ACKNOWLEDGMENTS

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[18] R. S. Mulliken, J. Chem. Phys. 23, 1997 (1955).

[19] F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, Phys. Rev. Letters 3, 420 (1959); I. Wieder and W. E. Lamb, Phys. Rev. 107, 125 (1957).