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Metastable Hydrogen Molecules. III. Hyperfine Structure of Orthohydrogen*

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The fine structure (fs) and hyperfine structure (hfs) of the $N=1$ rotational level of a single vibrational state of the $(1\sigma_g, 1\pi_u)c\,^3\Pi_u$ state of orthohydrogen has been measured by the molecular-beam magnetic-resonance method. Six independent frequency intervals have been measured to a precision of better than one part per million. The theory of fs and hfs, as developed by Fontana, Chiu, Jette, and Cahill has been used to fit the energy levels with four accurate, independent constants: the spin-orbit fs constant, $A=-3717.12$ MHz; the spin-spin fs constant, $B_0-\sqrt{6B_2}=9562.50$ MHz; the combined orbital and Fermi contact hfs constants, $\frac{1}{2}a+a_F=463.77$ MHz; the dipolar hfs term, $c-3d=104.18$ MHz; and the fifth, very much less accurately determined, orbital hfs constant, $a=26.6$ MHz. The Fermi contact constant $a_F=450.5$ MHz agrees remarkably closely with the value 440.1 found in H_2^+ by Jefferts. This indicates that the contact hfs of this state arises largely from a single core electron which is virtually the same as in H_2^+. The agreement between experimental energy levels and the theoretical fit is very good. The deviations are at worst 20 kHz, only a few parts per million in the measured intervals. If the previously measured fs of the $N=2$ state is used, the spin-spin constants become $B_0=-1420$ MHz, $B_2=-4480$ MHz. The spin-orbit constants for the $N=1$ and $N=2$ levels disagree by 3%. The constants $\frac{1}{2}a+a_F$ and $c-3d$ disagree by several percent with *a priori* calculations by Jette. The level of discrepancies among different experimental and theoretical results is an order of magnitude larger than can be obtained within the framework of the pure case-*b* coupling scheme. Evidence is found for nonadiabatic transitions of a new type for molecular-beam experiments. The discovery of new transitions proves that there is more than one metastable vibrational level of the $c\,^3\Pi_u$ state of H_2. It is likely, although not certain, that the present data are from the lowest ($v=0$) level.

I. INTRODUCTION

Quite some time ago, one of the authors found evidence that the $c\,^3\Pi_u$ state of H_2 has at least one metastable vibrational level.[1] Radio-frequency resonances in one rotational level ($N=1$) of orthohydrogen verified this hypothesis and gave preliminary values for the Landé g factors in both levels and the fine-structure (fs) separations in $N=2$ of parahydrogen.[2] Precise values for two fs separations in $N=2$ were then measured.[3] Preliminary values for two transitions between hyperfine levels in $N=1$ were reported.[4]

Lifetime measurements showed variations among different fs levels.[5] This was interpreted as evidence for an extremely weak forbidden predissociation of the $c\,^3\Pi_u$ state. It was reasoned that only even-N rotational levels of parahydrogen and odd-N levels of orthohydrogen are metastable.[5] Herzberg's discovery[6] of absorption of light by H_2 $c^3\Pi_u$ verified this hypothesis. Further measurements of lifetimes of fs levels have been made by the authors and by Johnson.[7] Additional measurements of g factors showed large deviations in orthohydrogen from the values predicted by pure case-b coupling.[7] $N=3$, 5 levels in orthohydrogen and $N=4$ in parahydrogen were also found to be metastable.[7]

A number of theoretical papers have been written on metastable hydrogen molecules. Fontana[8] worked out a theory of the fine structure. He obtained fortuitously good agreement between experimental results in MII[3] and a simple model. In the model, the inner electron of H_2 is reduced to a point charge, and the outer electron is hydrogenic. Chiu recalculated the theory of the fs.[9] She found an error in Fontana's work that destroyed the agreement between experiment and what appears to be an oversimplified model. With a relatively crude wave function, she obtained agreement within 20% between calculated[10] and observed[3] fs constants. Recently, Jette[11] has repeated the fs calculations with a better wave function.

Chiu[9] also has calculated the matrix elements for the forbidden perturbation which predissociates metastable H_2. She has obtained qualitative agreement with experimental results.[4,7] Browne and Bottcher also have worked on the theory of the decay of metastable H_2.[12] Freis and Hiskes[13] have made quantitative calculations of the radiative-decay probability of each vibrational level of H_2 $c\,^3\pi_u$. Browne, and Wahl, Zemke, and Lykos[14] have calculated wave functions for the c state.

The theory of molecular hyperfine structure is due to Frosch and Foley.[15] Mizushima and Frey[16] and Chiu[17] applied this theory to the hyperfine structure of orthohydrogen. Chiu's expressions disagreed with those of Mizushima and Frey. She also calculated the cross terms between the Zeeman and hf interactions. It is these terms that are responsible for the large changes in the g factors from the simple pure coupling case. Jette and Cahill[18] corrected an error in Chiu's calculation. Her corrected calculation[17] and their results[18] agree with each other and with experimental measurements of the g factors.[19] Jette and Cahill's treatment has been extended to give the Zeeman effect at all magnetic fields.[19] Recently, Jette[11] has repeated the calculations with the wave function of Wahl, Zemke, and Lykos.[14] Freed[20] has treated the theory of hyperfine interaction in molecules between cases a and b.

Herbig[21] has speculated that metastable H_2 may be involved in the source of diffuse interstellar bands. The possible use of metastable H_2 in fusion devices has been considered by Freis and Hiskes.[13] Varney and Morgan, Berkner, and Pyle[22] report evidence for formation of metastable beams of hydrogen molecules by charge exchange neutralization. Herzberg[6] has found evidence for laser action in emission spectra which go down to the c state.

Khare[23] has calculated the cross section for excitation of the c state by electron impact. Experimental cross sections have been reported in MI, by Cĕrmák[24] and by Clampitt and Newton.[25] The observation of resonances in elastic electron scattering from H_2 by Golden and Bandel[26] and by Simpson, Kuyatt, and Mielczarek[26] has led to investigation of resonant inelastic scattering by a large number of experimenters.[27] The $c\ {}^3\pi_u$ state is believed to play a role as an exit channel for these resonances. However, the closeness in energy of the vibrational levels of $c\ {}^3\pi_u$ and $a\ {}^3\Sigma_u^+$ has made it difficult to make a clear-cut separation of the roles of the two states.[28] Recent observations of metastable molecule production with a high-resolution bombardment apparatus by Pichanick[29] may help to resolve the problem.

The metastable hydrogen molecule has been used by Cĕrmák and co-workers[24] to study Penning reaction in molecules.

An important related experiment by Richardson, Dehmelt, and Jefferts[30] gives the hfs of the ${}^2\Sigma_g^+$ ground state of H_2^+. This is the ionic core which accounts for much of the hfs of metastable H_2.

This article presents a complete set of measurements of the fs and hfs of a single rotational level of orthohydrogen, $N = 1$. Indications of an additional metastable vibrational level are given. The need for measurements is twofold. First, the theoretical calculations have been flawed by errors. Second, the assumptions of pure case-b coupling overlook finer interactions that only experiment can detect at present.

II. METHOD AND APPARATUS

The methods and apparatus were described in MI and MII. Briefly described, the molecular-beam magnetic-resonance experiment was designed especially to study short-lived metastable molecules. Improvements in the apparatus included (i) a thoriated tungsten filament for longer lifetime, (ii) a palladium leak for purer hydrogen, and (iii) an improved transition region, to avoid rf interference. One pen of a two-pen recorder recorded frequency, as it was taken from a frequency-meter digital-to-analog converter combination. The other pen recorded the detector output, to give a simultaneous plot of "flop" and frequency. In the most recent measurements, frequency scanning and data recording were under the control of a small computer, which was interfaced to the experiment by Buckner and co-workers.[31]

Natural hydrogen, which is 75% ortho, was used.

III. RESULTS

A. Intervals

Preliminary results[4] in orthohydrogen gave two uhf lines: $\Delta J = 0$, $J = 2$; $\Delta F = \pm 1$; $F = 3 \leftrightarrow F = 2$, $f = 707.55 \pm 0.03$ MHz, and $F = 2 \leftrightarrow F = 1$, 462.44 ± 0.06 MHz. A search was made for other uhf and high-frequency ($f \sim 5$–8 GHz) lines, $\Delta J = \pm 1$, $\Delta F = 0, \pm 1$, $\Delta m_F = \pm 1$. These searches produced many high-frequency lines (see Table I). A combination of low signal-to-noise ratio and lack of understanding of the Zeeman structure made identification ambiguous. The perfection of the theory of the Zeeman structure[17–19] made identification of the quantum numbers (J, F, m_F) certain. Once the fs and hfs separations were roughly known, very accurate knowledge of the Zeeman effect was used in the final data processing. The Zeeman pattern was fit by solving for the energy levels in a finite magnetic field.[19] By an iterative process,[32] an assumed magnetic field was varied to give the best fit to the lines and to determine the correct zero-field intervals. Enough transitions were found to give a complete set of energy levels for o-H_2, $N = 1$: $J = 1$, $F = 0, 1, 2$; $J = 0$, $F = 1$; and $J = 2$, $F = 1, 2, 3$ (see Fig. 1 and Table I).

By a method developed by Wik,[33] a set of parameters was used to fit the observed intervals. It was found to be impossible to fit the preliminary experimental intervals for $J = 2$. The discrepancy between theory and experiment was several MHz. A continued search revealed that there were *two* sets of transitions with the same quantum numbers

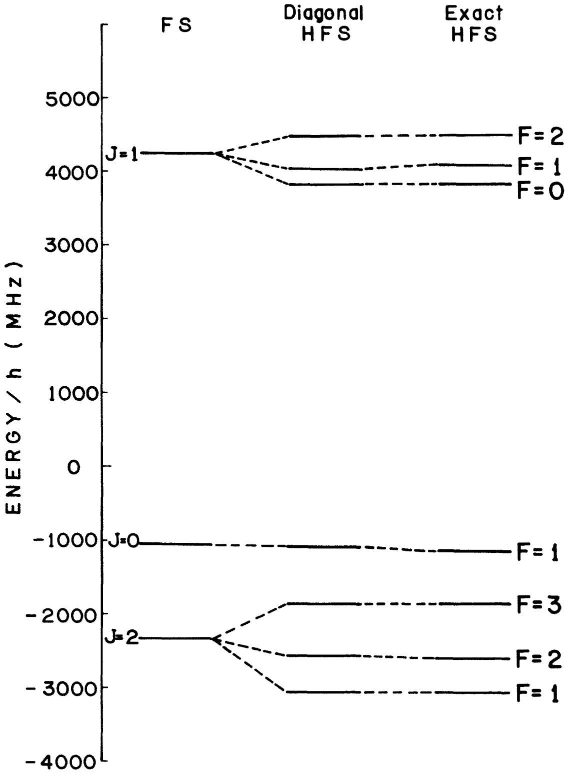

FIG. 1. Energy levels of the hydrogen molecule in the $c\,^3\Pi_u$ state, $N=1$ rotational quantum number. Three separate degrees of interaction are shown. FS shows the levels with fs turned on. Diagonal HFS shows the levels with only diagonal hfs interactions turned on. Exact HFS is the result of an exact diagonalization of the combined hfs and fs Hamiltonian. The exact HFS results are indistinguishable from experimental results on the scale of this drawing.

$J=2$: $F=3 \rightarrow F=2$ and $F=2 \rightarrow F=1$. Both sets of transitions had identical Zeeman patterns, but had zero field frequencies (see Tables I, IV, and Fig. 2) which differed by about $2\frac{1}{2}\%$. It was evident that two different metastable vibrational levels were being observed experimentally.

It was possible to find a complete set of energy levels which gave an excellent fit between theory and experiment (see Table II). In addition, a completely consistent set of microwave and redundant uhf transitions was found, which made it certain that the intervals all belonged to the same vibrational level.

B. Intensities

The relative amplitudes of the individual Zeeman components of a transition usually furnish confirmation of the assignment in molecular-beam experiments. The intensities usually are roughly proportional to the change in magnetic "moment" $\mu \approx dE/dB = g_S m_S + g_N m_N + g_I m_I$ of the molecule in the high fields of the deflecting magnets. The connection between the states at low fields (transition region) and high fields (deflection regions) is made by means of a correlation diagram.[34] The noncrossing rule, which assumes adiabatic transitions, prohibits the crossing of levels with the same value of m_F.

A comparison between observed and predicted intensities revealed discrepancies for several transitions. In particular, some transitions were found where no intensity was expected.

C. *g* Factors

Another discrepancy between theory and experiment arose from the Landé g factors.[7,19] Particularly worth noting is the $J=0$, $F=1$ level which has no electronic angular momentum in pure case-*b* coupling. It has a theoretical g factor of -0.003 and an observed value of -0.170 ± 0.005. A complete discussion of the Zeeman effect of metastable hydrogen molecules is given elsewhere.[19]

IV. DISCUSSION

A unique feature of the hydrogen molecule is that we can expect a precise comparison between experimental results and calculations by means of *a priori* wave functions. Experimental results are

TABLE I. Zero-field transition frequencies for metastable H_2.

f (MHz)	Standard error (MHz)	Assignment of angular momenta $(N', J', F' \leftrightarrow J, F, N)$ J'	F'	J	F	$N'=N$	Vibrational assignment (tentative)
278.35	~0.1	1	0	1	1	1	0
384.25	~0.1	1	1	1	2	1	0
450.6	~0.1	2	1	2	2	1	1
462.44	0.06	2	1	2	2	1	0
581.9	~0.5	4?	4?	4?	5?	3?	0?
707.55	0.03	2	2	2	3	1	1
725.1	~0.1	2	2	2	3	1	0
4928.003	0.01	2	...	1	...	2	0?, 1?
4937.337	0.0003	0	1	1	0	1	0
5150?							
5215.684	0.0007	0	1	1	1	1	0
5599.950	0.0013	0	1	1	2	1	0
5612?							
5898.105	0.012	3	...	2	...	2	0?, 1?
5944.6	~0.5	3	4	4	4	3	0
5975?							
6023?							
6110?							
6135?							
6142?							
6203?							
6208?							
6269?							
6295?							
6331?							
6348.719	0.0008	2	3	1	2	1	0
6357?							
6689.561	0.0015	2	2	1	1	1	0
6873.649	0.002	2	1	1	0	1	0
7073.830	0.0012	2	2	1	2	1	0
7152.000	0.001	2	1	1	1	1	0
7536.263	0.002	2	1	1	2	1	0

FIG. 2. Comparison of experimental results for two transitions with the same sets of angular momentum quantum numbers. This figure shows the identical structure of the lines, when taken at the same magnetic field. The ordinates are the oscillator frequency in MHz.

first compared with a parametrized theory. The parameters, or molecular constants, are fit to the experimental data. The values of the constants are then calculated *ab initio* from the Schrödinger equation.

A. Quality of Fit Between Experimental Data and Theory

Table II shows the comparison between experimental energy levels and those calculated from the best theoretical fit with the expressions of Fontana,[8] Chiu,[17] and Jette and Cahill.[18] The round-off error from the iterative computer-fitting routine of a few kilocycles can be expected. The deviations between theory and experiment seem to be within these errors, except for the $J=2$: $F=3$, 1 levels, where the discrepancies are 8 and 19 kHz, respectively. This excellent fit is partly due to the six constants which were available to fit the seven energy levels. Nevertheless, our experience with an incorrectly assigned transition (see Sec. III A) showed that the theory cannot be stretched to fit a false set of levels. This excellent agreement should be taken as a confirmation of the parametrized theory.[8,17,18]

B. Accuracy of Fitted Constants

The question now arises as to the accuracy of the constants. First, consider the hfs interaction constants. The combined orbital and Fermi contact hfs constants $\frac{1}{2}a+a_F$ and the dipolar term $c-3d$

TABLE II. Comparison of calculated and experimental energy levels.

J,F	Experimental energy levels (MHz)	Calculated energy levels (MHz)	Deviation (kHz) experimental − calculated Present[a]	Least squares[b]	Corrected[c]
1,2	4482.749	4482.752	−3	−7	−7
1,1	4098.483	4098.480	3	13	13
1,0	3820.136	3820.142	−6	−5	−5
0,1	−1117.201	−1117.200	1	0	0
2,3	−1865.970	−1865.973	3	−2	−2
2,2	−2591.081	−2591.089	8	3	3
2,1	−3053.514	−3053.495	−19	−1	−1
Sum of squares		$\sum\Delta_i^2$	489	257	256

[a] Difference of experimental and calculated energy levels from this table.

[b] A least squares fit.

[c] A least squares fit after a Van Vleck transformation was made to correct for perturbation of other rotational levels.

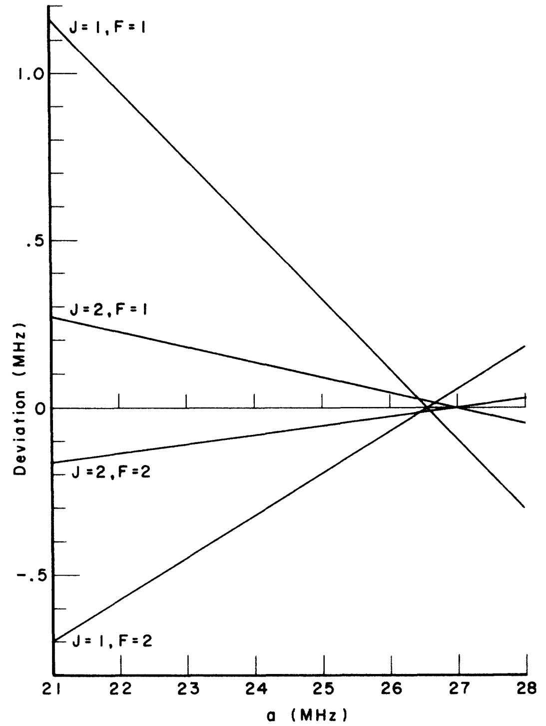

FIG. 3. Deviation of calculated terms from experimental values for different values of the hfs constant a. All other constants were optimized for each value of a. It can be seen that no unique value of a exists to give a best fit to the data. The value of $a = 26.6$ MHz was used for a best fit. The effect of the uncertainty in a on other constants is given in Table III.

enter into the diagonal matrix elements of the hfs interaction and are thus known relatively accurately. The off-diagonal term $-\frac{1}{2}a + a_F$ only has a small higher-order effect on energy levels (see Fig. 1). The individual terms a, a_F must be obtained by adding or subtracting the poorly known off-diagonal term; Fig. 3 compares the quality of theoretical fits for different values of a. It is clear that no unique value of a exists to give an optimal fit to the data. From the lack of fit alone, an error in the constant $a \sim 1$ MHz would not seem unreasonable.

The correctness of the constants cannot be tested by the goodness of fit alone. Various higher-order perturbations can cause a shift in the energy levels of a fraction of a percent, or ~1 MHz, which could shift a by as much as several MHz. Until experimental data is available from other rotational levels, a more precise statement cannot be made about the accuracy of the constants. Table III shows the effect on other constants from a shift in a by the arbitrary amount of 1 MHz. For purposes of comparison, uncertainties due to molecular wave functions and lack of vibrational assignment are approximately several percent, and rotational effects are a few tenths of a percent.

The fs constants A (spin-orbit) and the linear combination $B_0 - \sqrt{6}B_2$ (spin-spin) are given by this experiment. Table III shows that these constants are only affected in a minor way by the uncertainty in the hfs constants. Likewise, the second-order perturbation of the rotational fs by spin changes these constants by a few hundredths of a percent.[10] (These corrections have been omitted from the treatment of results.) On the other hand, the fs measurements in MII for the $N = 2$ levels gave independent values for A and a different linear combination $B_0 + \sqrt{6}B_2$. The values for these constants are shown in Table III, which also lists theoretical calculations for comparison.

The two values for A disagree by approximately $2\frac{1}{2}\%$, about an order of magnitude larger than the expected effect of rotational distortion.[3] However the discrepancy is of the same order of magnitude as the expected shift of a single vibrational quantum.[3] Although it is certain that the $N = 1$ results came from a single vibrational level, there is no evidence to exclude either or both $N = 2$ transitions coming from a different vibrational state. Although the assignment of angular momentum quantum numbers (J, F, and m_F) is unambiguous, the vibrational quantum number is uncertain by about one unit.

TABLE III. Fine- and hyperfine-structure constants for $N = 1$ and $N = 2$.

Values obtained from the present experiment, $N = 1$

Constant	Value (MHz) Experiment	Value (MHz) Theory	Shifts caused by changing a by 1 MHz Shift (MHz)	Shifts caused by changing a by 1 MHz % change
A	−3717.120	−4100[a]	−0.024	0.0006
$B_0 - \sqrt{6}B_2$	9562.488	8100[a]	0.432	0.005
a	26.6	17.44[a] 17.12[b] 21.98[c]	1.0	4.
$a_F + \frac{1}{2}a$	463.767	553.99[a] 553.83[b] 482.13[c]	0.054	0.01
a_F	450.479	545.27[a] 545.27[b] 471.14[c]	0.445	0.1
$c-3d$	104.177	73.82[a] 75.11[b] 97.98[c]	−0.253	0.2

Values obtained from $N = 2$, or by combining both sets of results[d]

Constant	Value (MHz)	Theoretical value
A	−3822.144	−4100[a]
$B_0 + \sqrt{6}B_2$	−12404.10	−10800[a]
B_0	−1420.807	−1330[a]
B_2	−4483.911	−3840[a]

[a] Reference 10 or Ref. 17.

[b] Reference 18. The same wave function was used as in Ref. 17.

[c] Reference 11.

[d] Because of uncertainty of vibrational assignments, all constants in this table are in doubt by several percent.

TABLE IV. Comparison of hyperfine interactions in hydrogen and its molecular ion (MHz).

Vibrational quantum number[a]	Fermi contact constant		Molecular hf interval $J=2$, $N=1$	
	$a_F(H_2)$	$a_F(H_2^+)=\frac{1}{2}b$	$F=1\leftrightarrow F=2$	$F=2\leftrightarrow F=3$
0	450.5	440.1	462.436 ± 0.005[b]	725.111 ± 0.005[b]
1		429.3	450.6 ± 0.1	707.55 ± 0.03
Ratio of interval or constant $f(1)/f(0)$		0.975	0.974[c]	0.976[c]

[a] Assignment for H_2 tentative.

[b] Intervals for $v=0$ were calculated from differences between high-frequency transitions. Results are in agreement with directly measured frequencies in Table I, but have higher precision.

[c] No corrections for second-order effects were made. The effects of these corrections would be 1 or less in the last decimal place of the ratios.

C. Comparison with the H_2^+ Core Model

The dominant term in the hfs interaction is the Fermi contact term[18]

$$H_F(H_2)=a_F(\vec{I}\cdot\vec{S}),$$

which arises from the H_2^+ core, where the corresponding term[30] is

$$H_F(H_2^+)=b(\vec{I}\cdot\vec{s}_1),$$

where $\vec{I}$ is the nuclear spin; $\vec{S}=\vec{s}_1+\vec{s}_2$ is the total electronic spin, the sum of the spin $\vec{s}_1$ of the inner electron, and the spin $\vec{s}_2$ of the outer electron. By an elementary calculation, $\vec{I}\cdot\vec{s}_1=\frac{1}{2}\vec{I}\cdot\vec{S}$, which gives the simple relation that $a_F=\frac{1}{2}b$.

From Jefferts's data,[30] we obtain the extrapolated values of b, which are shown with the corresponding calculated values of a_F in Table IV. The value obtained from the $v=0$ vibrational level of H_2^+, $a_F(H_2^+)=440$ MHz is in remarkably good agreement with the present value $a_F(H_2)=450.5$. This is a striking confirmation of the McDonald model,[3,35] which treats the excited states of H_2 as a Rydberg electron surrounding a H_2^+ core.

D. Vibrational Assignments

It is interesting to compare the ratio of hfs constants for successive vibrational levels in H_2^+ with the same ratio for two hfs transitions in H_2 (uncorrected for second-order effects) in Table IV. There is striking agreement among the three ratios. One would expect this if the hf transitions in H_2 were in two neighboring vibrational levels; the equilibrium internuclear distances, force constants, and vibrational wave functions for excited H_2 and the ground state of H_2^+ are closely the same.

In MI and MII, it was assumed that only the lowest ($v=0$), or possibly the lowest two ($v=0$ and $v=1$), vibrational levels are metastable. The arguments in favor of this hypothesis follow.

The first process which causes the c state to decay is forbidden magnetic dipole radiation to the $a\,{}^3\Sigma_u^+$ repulsive state. Freis and Hiskes[13] have calculated the radiative decay probability to be 10^3 sec^{-1} for the $v=0$ level and to be $\sim 10^4$ sec^{-1} for higher levels. The second mechanism is a forbidden predissociation. Chui found that the predissociative decay probability has no marked dependence on N, the rotational quantum number.[9] However, as the vibrational quantum number gets larger, the overlap increases between ${}^3\pi$ and ${}^3\Sigma$ vibrational wave functions. This would increase the decay probability and shorten the lifetime. Herzberg verified this in his absorption experiments.[6] Therefore, it seems most likely that the complete set of transitions in $N=1$ is in the lowest vibrational level $v=0$. The additional two hfs transitions are most likely $v=1$. The transitions in $N=2$ are still uncertainly assigned, probably $v=0$ or $v=1$.

It would be desirable to clear away the ambiguity in vibrational assignment. Although *ab initio* calculations are not yet fine enough to make these assignments important, one can foresee the need for this precision in the future.

E. Intensities

The cause for the unexpected relative intensities among Zeeman components was found in "anticrossings" between energy levels.[19] Two levels with the same value of m_F come so near to each other that nonadiabatic transitions occur. In the extreme case that the repulsion is negligibly small, diabatic transitions occur. That is, the levels always cross. The Landau-Zener model[36] predicts that transitions with a repulsion much larger than 40 MHz should be adiabatic.[19] Transitions with repulsions much smaller than 40 MHz should be diabatic. Transitions with repulsions ~40 MHz should be mixed in nature. The 5600 MHz transition (see Table V) is an example where the intensities seem close to the diabatic case. It should be noted that the repulsions for the "crossings"

TABLE V. The 5600-MHz transition.

Transition	1	2	3	4
$J=1$, $F=2$, $M=$	1	0	0	1
$J=0$, $F=1$, $M=$	0	−1	1	0
Change in magnetic moment (μ_B)				
adiabatic[a]	1.97	2.02	0.45	2.46
diabatic[a]	1.59	2.49	1.92	2.08
Relative observed intensities	15	24	24	18

[a] These terms refer only to the anticrossings at $\mu_B B/h=486$, 835, or 903 MHz for the levels $J=0$, $F=1$, $m_F=1,0$, respectively. All other levels are assumed to have purely adiabatic transitions. See Ref. 19 for a more detailed and extensive discussion.

involved in the 5600 MHz transition are 1.7 and 19.4 MHz. Thus the theory[19] is in qualitative agreement with experiment. The deflection fields were not designed to make a quantitative test of the theory. Therefore a more precise interpretation cannot be made on the experiments.

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

[2] W. Lichten, Phys. Rev. 120, 848 (1960), Paper I of this series to be called M I.

[3] W. Lichten, Phys. Rev. 126, 1020 (1962), to be called M II.

[4] W. Lichten, Bull. Am. Phys. Soc. 7, 307 (1962).

[5] W. Lichten, Bull. Am. Phys. Soc. 7, 43 (1962).

[6] G. Herzberg, Sci. Light (Tokyo), 16, 14 (1967).

[7] P. R. Brooks and W. Lichten (unpublished). g factors are reported in Ref. 19. A single lifetime of $\tau = 1.02 \pm 0.05$ msec for metastable o-H_2, p-H_2, D_2, and HD has been reported by C. E. Johnson [Bull. Am. Phys. Soc. 16, 533 (1971)] and in a private communication.

[8] P. R. Fontana, Phys. Rev. 125, 220 (1962).

[9] L. Y. C. Chiu, J. Chem. Phys. 40, 2276 (1964).

[10] L. Y. C. Chiu, Phys. Rev. 137, A384 (1965).

[11] A. N. Jette (unpublished).

[12] J. C. Brown and C. Bottcher (unpublished).

[13] R. P. Freis and J. R. Hiskes, Phys. Rev. A 2, 573 (1970).

[14] J. C. Browne, J. Chem. Phys. 40, 43 (1964); A. C. Wahl, W. T. Zemke, and P. G. Lykos, *ibid.* 51, 5635 (1969).

[15] R. A. Frosch and H. M. Foley, Phys. Rev. 88, 1337 (1952).

[16] M. Mizushima and D. A. Frey, Phys. Rev. 128, 2683 (1962).

[17] L. Y. C. Chiu, Phys. Rev. 145, 1 (1966); 159, 190 (1967).

[18] A. N. Jette and P. Cahill, Phys. Rev. 160, 35 (1967). Both this reference and the one following contain theoretical expressions for the fs and hfs.

[19] W. Lichten, Phys. Rev. A 3, 594 (1971). The author is indebted to Saul Epstein, for pointing out that Eq. (12) of this paper had been derived previously by I. F. Kovalev and L. S. Majanc, Dokl. Akad. Nauk SSSR 108, 175 (1956) [English transl.: Appendix F of the University of Wisconsin Technical Summary Report No. 948, 1968 (unpublished)].

[20] K. F. Freed, J. Chem. Phys. 45, 4214 (1966). For a treatment of his in case-c coupling, see K. F. Freed, *ibid.* 45, 1714 (1966).

[21] G. H. Herbig, Astrophys. J. 137, 200 (1963).

[22] R. N. Varney, Phys. Rev. 157, 113 (1967); T. J. Morgan, K. H. Berkner, and R. V. Pyle, Phys. Rev. Letters 26, 602 (1971).

[23] S. P. Khare, Phys. Rev. 157, 107 (1967).

[24] V. Cěrmák, J. Chem. Phys. 44, 1318 (1966). See also H. Hotop, F. W. Lampe, and A. Niehaus, J. Chem. Phys. 51, 593 (1969).

[25] R. Clampitt and A. S. Newton, J. Chem. Phys. 50, 1997 (1969).

[26] D. E. Golden and H. W. Bandel, Phys. Rev. Letters 14, 1010 (1965); J. Arol Simpson, C. E. Kuyatt, and S. R. Mielczarek, *ibid.* 12, 293 (1964); J. Chem. Phys. 44, 437 (1966).

[27] H. G. M. Heideman, C. E. Kuyatt, and G. E. Chamberlain, J. Chem. Phys. 44, 440 (1966); J. T. Dowell and T. E. Sharp, *ibid.* 47, 5068 (1967); A. Weinsgartshofer, H. Ehrhardt, and F. Linder, *Sixth International Conference on the Physics of Electronic and Atomic Collisions. Abstracts of Papers* (MIT Press, Cambridge, 1969), p. 91; R. I. Hall, A. Dumas, J. Mazeau, and J. Reinhardt, *ibid.*, p. 95; H. Ehrhardt and A. Weingartshofer, Z. Physik 226, 28 (1969); R. I. Hall, J. Mazeau, J. Reinhardt, Phys. Letters 30A, 427 (1969); 31A, 145 (1970).

[28] S. Trajmar, D. C. Cartwright, J. K. Rice, R. T. Brinkmann, and J. Kuppermann, J. Chem. Phys. 49, 5464 (1968).

[29] F. Pichanick (private communication).

[30] H. G. Dehmelt and K. B. Jefferts, Phys. Rev. 125, 1318 (1962); C. B. Richardson, K. B. Jefferts, and H. G. Dehmelt, *ibid.* 165, 80 (1968); K. B. Jefferts, Phys. Rev. Letters 20, 39 (1968); 23, 1476 (1969).

[31] A. Buckner, senior essay (Yale College, 1970) (unpublished).

[32] R. Reno, Ph. D. thesis (Yale University, 1971) (unpublished). Details of experimental methods and computer programs are given here.

[33] T. Wik, senior essay (Yale College, 1968) (unpublished).

[34] See Ref. 19, Fig. 1.

[35] See Ref. 41 of M II for references. Some recent references are R. S. Mulliken, J. Am. Chem. Soc. 86, 3183 (1964); and A. U. Hazi and S. A. Rice, J. Chem. Phys. 47, 1125 (1967).

[36] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, 2nd ed. translated by J. B. Sykes and J. S. Bell, (Addison-Wesley, Reading, Mass., 1965), pp. 328–329.