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Fourier transform spectroscopy analysis of the 3d-triplet complex visible emission spectra of H₂

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An investigation of the triplet 3d-complex of H₂, the $g(3d)^3\Sigma_g^+$, $i(3d)^3\Pi_g$, and $j(3d)^3\Delta_g$ and the nearby $h(3s)^3\Sigma_g^+$ electronic states, has been performed. The $3s,3d \rightarrow c(2p)^3\Pi_u^-$ visible emission spectra have been obtained with a low pressure discharge lamp and recorded with a Fourier transform spectrometer. Transition wave numbers and rotational energy levels are given for $v = 0-3$ of the four states. An effective Hamiltonian is used to fit the data, which shows the rotational breakdown of the Born–Oppenheimer approximation due to the L -uncoupling effect. The eigenvectors obtained from this model provide considerable insight into the nature of the 3d-complex. Furthermore, the model shows the mixing between the 3d states and the $h(3s)^3\Sigma_g^+$ state which is particularly strong for lower v values. Molecular constants, coupling parameters, and term values are also given.

I. INTRODUCTION

Although H₂ is the simplest neutral molecule, it does not necessarily follow that all of its excited-state energy levels are well understood. This fact results primarily from the inadequacy of the Born–Oppenheimer approximation for these excited states and hence the importance of vibrational–electronic and rotational–electronic interaction. Such interactions lead to irregularities in line positions and intensities in the optical spectrum of H₂ which render assignments difficult. In particular, these remarks apply to one of the numerous intriguing problems in the electronic spectra of H₂, the $3s,3d$ - Σ,Π,Δ complex of states.

The $3s, 3d$ states, $h(3s)^3\Sigma_g^+$, $g(3d)^3\Sigma_g^+$, $i(3d)^3\Pi_g$ and $j(3d)^3\Delta_g$ (Fig. 1), need special treatment because the electronic energy separations between the individual states are much smaller than, or of the same order of magnitude as, the rovibrational energy separations. Consequently the rotation of the molecules induces a breakdown of the Born–Oppenheimer approximation. This effect is known as L -uncoupling since it corresponds to a reduction in the degree of coupling between the electronic angular momentum L and the molecular axis of the molecule. Thus, these states have a coupling intermediate between Hund's cases b and d , the ordinary Born–Oppenheimer approximation fails and the final computed states become strongly interacting.

The first extensive work on the triplet states of the hydrogen molecule was made in the 1930's by Richardson *et al.*¹ Optical transitions involving the $3s,3d$ -triplet complex of states were observed and partially assigned. Shortly thereafter, Davidson² made calculations to determine the energy levels of these states and obtained satisfactory agreement between theory and experiment. In the 1950's, Dieke *et al.*^{3,4} obtained spectra with higher resolution and improved our knowledge of the positions of the optical transitions from the states involved in the $3s,3d$ -triplet complex. Furthermore,

the specific problem of the evaluation of molecular constants for L -uncoupled states has been extensively studied,^{1,2,5-9} and successfully applied to the 3d-singlet complex case in H₂.^{2,10,11} The results for these states were obtained empirically by using the uncoupled levels as adjustable parameters. A similar treatment was attempted with quite good accuracy to the 3d-triplet parity levels by Ginter.¹² Jost *et al.*¹³ have reported for the first time the most consistent set of molecular constants for the four states involved in the $3s,3d$ -triplet complex of H₂. These authors, using Dieke's tables, extended the previous study of Ginter¹² to the + parity levels. They have established a reasonable background for the analysis of the Zeeman effects in the $3s,3d$ -triplet complex. Eigenvectors have been calculated to interpret experimental measurements of the g factors, but, as noted more completely in this work, they cannot be expected to be exact and the theoretical descriptions are not yet completely resolved. The same conclusion was reached when the fine structure calculation was made using the same theoretical model and data by Lichten *et al.*¹⁴ Until now, the agreement between theoretical predictions and observed optical transitions remains unsatisfactory, as pointed out by several authors.¹²⁻¹⁵

In order to clarify the situation, we decided to record by Fourier transform spectroscopy an uncongested spectrum of H₂ using a low pressure discharge. Because only specific electronic transitions are observed by this method, the rotational analysis is considerably simplified and becomes unambiguous.¹⁶ Furthermore, the high resolution visible Fourier transform spectrometer gives accurate line positions. A new fitting procedure was used to generate an improved set of molecular constants. The agreement between our experimental and theoretical results is satisfactory, even for the highly perturbed Kronig + parity levels. Molecular constants and energy levels for $v = 0-3$ of all states $3s,3d$ are given. The molecular constants for the $c(2p)^3\Pi_u^-$ lower state were obtained using the rotational line positions of the $a(2s)^3\Sigma_g^+ - c(2p)^3\Pi_g^-$ transition given by Dabrowski and Herzberg¹⁷ from the spectra obtained by Fourier transform infrared spectrometry. We must mention that laser spectroscopy

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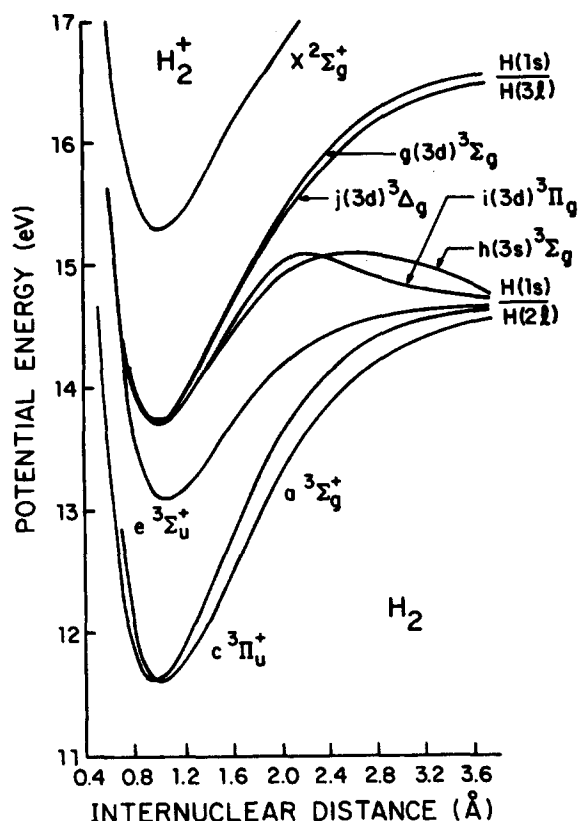


FIG. 1. Some electronic states of H₂ showing those relevant to this work. The curves are taken from Sharp, Ref. 31.

copy is now possible for the study of such transitions, but this kind of experiment is very time consuming if high resolution is attempted. The advantage of Fourier transform spectroscopy is that one experiment is sufficient to record a large spectral range when, of course, the emitted intensity is sufficiently strong.

II. EXPERIMENTAL

We used a low pressure discharge connected to a Fourier transform spectrometer. This discharge, described in a previous work,¹⁸ is similar to a Penning ionization discharge. The design of the apparatus is made so that the plasma is confined between two alumina cathodes of 1 cm diam, separated by 1 cm. The two cathodes are water-cooled. The presence of a magnetic field of 0.1 T makes it possible to run the source at a pressure as low as 10⁻⁴ Torr. The source was run at around 300 V, 400 mA. The Fourier transform spectrometer is a BOMEM DA3 operating between 15 000 and 20 500 cm⁻¹. Recording time was 2.5 h. The resolution is 0.1 cm⁻¹. The detector was an avalanche silicon photodiode, with a (Corning 1-75) filter placed before the detector.

New assignments of emission lines in the visible transitions of H₂ molecule have been made (Fig. 2). In this present work, only emission lines readily identified as belonging to the *j, i, g, h* → *c* transitions have been measured. They are collected in Tables I–IV, respectively. The spectra cover the range from 15 500 to 20 500 cm⁻¹. Dieke's compilation of term values for H₂ has been used for predicting the positions

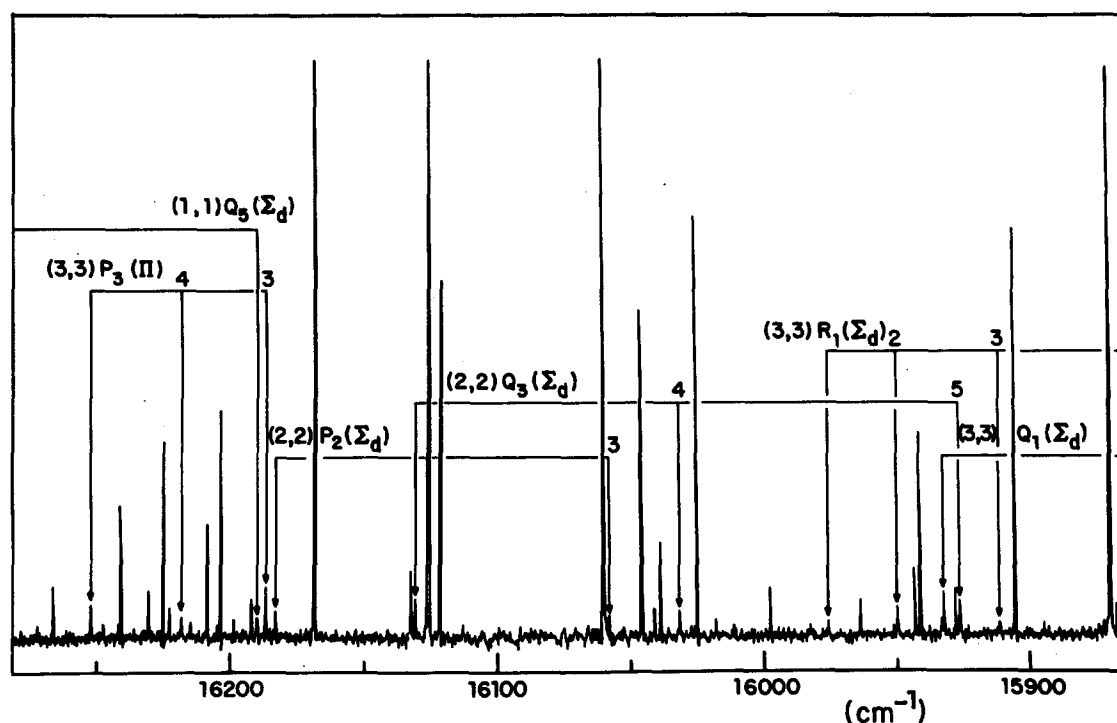


FIG. 2. Section of the visible emission spectrum of H₂ obtained from the low pressure discharge and recorded by a Fourier transform spectrometer. Some of the lines of the 3s,3d → (2p)³Π_u transitions are shown. The state in bracket indicate the origin of the transition.

TABLE I. Wave numbers of the lines of the $j(3d)^3\Delta_g-c(2p)^3\Pi_u$ system of H₂ (cm⁻¹).

Band	<i>N</i>	<i>P</i>	<i>Q</i>	<i>R</i>
(0-0)	1			17 572.375
	2		17 451.611	17 669.768
			17 467.034	17 717.039
	3	17 271.569	17 489.872	17 765.121
		17 287.264	17 537.108	17 850.389
	4	17 251.876	17 527.472	17 251.932
				17 855.889
	5	17 233.178	17 562.417	
		17 318.778	17 686.123	
	6	17 338.459	17 754.327	
(1-1)	1	17 426.294		
				17 431.568
	2		17 311.100	17 509.012
			17 316.566	17 529.042
	3	17 139.767	17 337.401	17 591.231
		17 144.765		17 633.897
	4	17 110.876	17 364.323	17 669.789
			17 407.456	17 739.540
	5	17 084.562	17 389.615	17 743.112
		17 127.103	17 459.657	
(2-2)	6	17 058.269		
	7	17 030.772		
	1			17 279.019
				17 280.666
	2		17 169.234	17 348.172
			17 171.276	
	3	17 006.377	17 184.477	17 416.461
			17 192.294	17 433.458
	4	16 969.277	17 200.142	17 481.564
		16 975.927	17 218.515	17 512.777
(3-3)	5	16 934.389	17 214.223	
		16 950.876	17 246.766	17 541.398
	6		17 273.737	
	1			17 129.926
				17 130.398
	2		17 025.417	17 186.018
			17 026.375	
	3	16 870.658	17 030.123	17 239.742
			17 033.228	17 244.837
	4	16 825.876		17 288.038
		16 827.102	17 040.805	17 304.141
	5	16 781.564	17 034.989	
		16 786.569	17 051.876	

of the observed bands. Note that only $\Delta v = 0$ bands which have more favorable Franck-Condon factors are present in the spectra. The triplet splitting is not resolved in any of the observed transitions. The first two ($^3\Delta_g-^3\Pi_u^-$ and $^3\Pi_g-^3\Pi_g^-$) consist of very widely spaced *P, Q, R* branches, each of them having a large Λ -type doubling. The expected intensity alternation in successive Λ -doubling pairs of a given branch is not present as previously stated.¹⁹ In the *R* and *P* branches, for both even and odd *N* the shortward components, assigned to the $-$ parity states, are by far the strongest and the longward ones, assigned to the $+$ parity states, are either weak or absent, while for the *Q* branches they are the strongest. The explanation of such an intensity distribution is given by the fact that the $c(2p)^3\Pi_u^+$ state is rapidly predissociated by the nearby $b(2p)^3\Sigma_u^+$ state. Despite this

TABLE II. Wave numbers of the lines of the $i(3d)^3\Pi_g-c(2p)^3\Pi_u$ system of H₂ (cm⁻¹).

Band	<i>N</i>	<i>P</i>	<i>Q</i>	<i>R</i>
(0-0)	1		17 125.076	17 199.259
			17 212.045	
	2	17 004.292	17 078.339	17 202.536
		17 091.303	17 248.453	17 441.359
	3	16 898.425		17 199.259
			17 261.325	17 498.128
	4	16 784.647	16 961.689	17 191.412
		17 023.554	17 260.658	17 546.921
	5		16 897.723	17 179.379
		16 966.908	17 252.664	
(1-1)	6		17 233.148	
	1			16 978.565
			16 988.675	17 138.889
	2	16 784.487	16 863.336	16 988.854
		16 873.463		17 218.515
	3	16 692.039	16 817.363	16 990.702
		16 852.192	17 047.158	17 283.100
	4		16 763.905	16 986.067
		16 820.281	17 056.643	17 335.231
	5	16 484.085		
(2-2)		16 776.287	17 055.479	17 377.899
	1		16 648.425	16 730.546
			16 684.925	
	2	16 539.203		16 746.628
		16 575.153	16 712.735	16 897.233
	3		16 582.776	16 753.334
		16 548.917	16 734.146	16 961.010
	4	16 367.768	16 537.119	16 752.556
		16 518.121		17 013.446
	5		16 485.185	
(3-3)			16 747.606	17 054.204
	1		16 365.446	16 445.778
			16 388.325	16 511.487
	2		16 341.356	16 465.554
		16 283.778		16 578.887
	3	16 186.554	16 309.478	16 476.125
		16 251.734	16 424.356	16 629.342
	4		16 425.145	
		16 218.223	16 428.675	16 678.566

effect, anomalous intensity distributions in the rotational lines are also observed because the transition moment vanishes for certain mixing coefficient of the $3d$ states.^{15,20} For example, in the (0,0) band of the expected $i(3d)^3\Pi_g-c(2p)^3\Pi_u^-$ system, the *P* 3 and *Q* 3 lines are absent although both *P* 2 and *P* 4, *Q* 2 and *Q* 4 are present. Other examples exist for the four systems in all observed bands. Also, our low pressure discharge clearly shows the breaking off of the rotational structure due to predissociation. Only levels belonging to $v = 0-3$ are observed except for the $g(3d)^3\Sigma_g^+$ state where we have assigned one transition attributed to the (4,4) band (*Q* 1 line at 15 520.037 cm⁻¹). Unfortunately, no other (4,4) band transitions are present in our recorded spectra.

III. ANALYSIS

To understand the triplet $3d$ -complex we should obtain a theoretical description of the observed spectra and report molecular constants for the states involved in this complex

TABLE III. Wave numbers of the lines of the $g(3d)^3\Sigma_g^- - c(2p)^3\Pi_u$ system of H₂ (cm⁻¹).

Band	<i>N</i>	<i>P</i>	<i>Q</i>	<i>R</i>
(0-0)	1	16 841.260	16 854.884	16 884.919
	2	16 734.146	16 764.164	16 834.296
	3	16 416.321	16 654.266	16 774.917
	4	16 243.072	16 536.946	
	5		16 416.421	16 643.045
	6			16 573.154
(1-1)	1	16 602.690	16 603.258	16 630.503
	2	16 488.051	16 515.516	16 584.746
	3	16 343.842		16 530.151
	4		16 304.025	16 469.903
	5	16 023.234	16 190.078	16 405.534
(2-2)	1	16 287.725	16 297.283	16 332.112
	2	16 187.473		16 294.883
	3	16 059.112	16 132.151	16 247.352
	4	15 915.856	16 032.154	16 192.295
	5		15 926.458	
(3-3)	1	15 913.388	15 932.073	15 976.148
	2		15 872.183	15 949.754
	3	15 716.382	15 795.212	15 910.792
	4	15 589.034	15 706.583	15 862.922
	5		15 610.881	

which have been corrected for *L*-uncoupling. Our approach is similar in spirit to that previously used by Freund and Miller¹⁰ to describe the singlet *3d* manifold. Since the fine structure is unresolved in the optical spectrum, and for Rydberg states of diatomic molecules with ¹Σ of ²Σ cores, the electronic angular momentum involved for *L*-uncoupling is that of the single Rydberg electron,²¹ we can treat the levels as if they were singlets. The states are all (quasi) Rydberg states, so a good approximation can be obtained by consider-

TABLE IV. Wave numbers of the lines of the $h(3s)^3\Sigma_g^- - c(2p)^3\Pi_u$ system of H₂ (cm⁻¹).

Band	<i>N</i>	<i>P</i>	<i>Q</i>	<i>R</i>
(0-0)	1	16 991.780	17 006.583	17 108.492
	2	16 885.816	16 987.383	17 160.867
	3		16 980.781	17 215.425
	4	16 743.162	16 977.382	
	5	16 683.783		
(1-1)	1	16 898.250	16 917.554	17 031.607
	2	16 802.376		17 086.583
	3		16 915.352	17 139.767
	4	16 688.325	16 913.465	17 190.544
	5	16 633.121	16 910.831	17 238.377
	6	16 579.062		
(2-2)	1			16 950.867
	2		16 841.637	17 004.478
	3	16 677.830	16 841.637	17 056.677
	4	16 625.759	16 841.637	
	5	16 575.153		
(3-3)	1			
	2		16 778.553	
	3	16 778.740		16 933.842
	4	16 525.609	16 798.110	16 982.778

ing that an electron in an hydrogenic *3d* (or *3s*) orbital is bound to an H₂⁺ core which is in its electronic ground state, little affected by the outer electron. Therefore the rotational quantum number *N* is used and the labels *P, Q, R* represent the Δ*N* = -1, 0, 1 transitions, respectively. Because the potential curves of the four states are very similar for *v* = 0-3 and the separations between electronic states are very small compared to the vibrational separation, we may assume that the vibrational quantum number *v* is a good quantum number. Also, the electronic orbital angular momentum is assumed to be equal to that of the outer electron, so we have *L* = 0 and 2 for the *3s* and *3d* states, respectively. The axial field of the core splits the *3s, 3d*-complex according to Δ yielding two ³Σ_g⁺, one ³Π_g, and one ³Δ_g states. The Π and Δ states have a *3d* character, while the two ³Σ_g⁺ are mixed *3s* and *3d*. The *3s* state will be involved in the rotational couplings, because an electrostatic coupling mixes the *3s* state with the (*3d*) Σ_g⁺ state which, in turn, is rotationally coupled to the other *3d* states. Wakefield and Davidson⁸ have previously calculated a significant coupling between the two ³Σ_g⁺ states. Thus, for describing an effective Hamiltonian which gives a close representation of our data for the *3s, 3d*-triplet energy levels in H₂, we choose a model similar to that used by Ginter,⁹ Jost *et al.*¹³ and Keiding *et al.*,¹⁵ but our treatment of the rotational interaction is different because new adjustable parameters are introduced.

As usual, when the spin effects are omitted, the rotational part of the Hamiltonian is written as follows:

$$H_{\text{Rot}} = B(R)R^2 = B(R)(N - L)^2.$$

R is perpendicular to the molecular axis *z*, so *R_z* = 0. Then we can rewrite:

$$H_{\text{Rot}} = B(R)(N^2 + L^2 - 2L_z^2 - (N^+L^- + N^-L^+)).$$

We used the $|nvNLA\rangle$ wave functions, where *n, v, N, L*, and *Λ* are the usual quantum numbers. Hence, within the same vibronic state, the matrix elements are

$$\begin{aligned} \langle nvNLA | H_{\text{Rot}} | nvNLA \rangle \\ = B_v [N(N+1) - L(L+1) - 2\Lambda^2], \end{aligned}$$

where *B_v* = $\langle nv | B(R) | nv \rangle$.

The coupling between different electronic states of the same *L* and *N* becomes

$$\begin{aligned} \langle n'v'NLA \pm 1 | H_{\text{Rot}} | nvNLA \rangle \\ = -W_1^{\Lambda, \Lambda'} [\Lambda(L+1) - \Lambda(\Lambda \pm 1)]^{1/2} \\ \times [N(N+1) - \Lambda(\Lambda \pm 1)]^{1/2}, \end{aligned}$$

where *W*₁^{Λ,Λ'} is the coupling parameter. The centrifugal interaction *D* is proportional to the operator *R*⁴. The matrix representation is most easily obtained by squaring the *R*² operator already used for the rotation, so the corresponding off-diagonal parameters are labelled *W*₂^{Λ,Λ'}. The electronic coupling of the two Σ_g⁺ states *3s* and *3d* is taken into account through the *N* independent *E*_Σ parameter. Finally, each electronic state is represented by the term energy *T* which represents the vibrational and electronic energies. To take into account the symmetry of states having Λ ≠ 0 we used the basis functions, as defined by Zare *et al.*²² as follows:

$$\Psi^\pm = 2^{1/2} (|nvNLA\rangle \pm |nvNL - \Lambda\rangle).$$

TABLE V. The effective L -uncoupling Hamiltonian has the following matrix representation in the \pm parity basis $(\Delta, \Pi, \Sigma_d, \Sigma_s)$, where $x = N(N+1)$, and the $+$ and $-$ signs correspond to the $+$ and $-$ parity levels, respectively.

Δ	Π	Σ_d	Σ_s
$T_\Delta + B_\Delta(x-2) - D_\Delta(x^2-4)$	$\begin{bmatrix} -2W_1^{\Delta,11} + 4W_2^{\Delta,11}(x+1) \\ T_{11} + B_{11}(x+4) - D_{11}(x^2+15x \pm 3x+8) \end{bmatrix} (x-2)^{1/2}$	$\begin{bmatrix} -W_1^{11\Sigma} + 2W_2^{11\Sigma}(x+5) \\ T_{\Sigma d} + B_{\Sigma d}(x+6) - D_{\Sigma d}(x^2+18x+36) \end{bmatrix} (6x)^{1/2}$	$\begin{bmatrix} E_\Sigma \\ T_{\Sigma s} + B_{\Sigma s}x - D_{\Sigma s}x^2 \end{bmatrix}$

For each value of N , we obtain a 6×6 Hamiltonian matrix consisting of two separate blocks, one 4×4 block representing the $+$ parity levels and one other 2×2 block for the $-$ parity ones (Table V). Thus we have a total of 17 parameters for each vibrational level.

For the $(2p) \ c^3\Pi_u^-$ lower state, we use the following traditional formula in Hund's case (a) basis set:

$$T_v(J) = T_v + B_v J(J+1) - D_v J^2(J+1)^2,$$

where T_v , B_v , and D_v are the vibronic origin, the rotational constant, and the centrifugal distortion constant, respectively.

IV. RESULTS AND DISCUSSION

The molecular constants for the $c(2p)^3\Pi_u^-$ state were obtained in a preliminary work by fitting the data from the infrared transitions $a(2s)^3\Sigma_g^+ \rightarrow c(2p)^3\Pi_u^-$ assigned by Dabrowski and Herzberg.¹⁷ They are listed in Table VI. The standard deviation (0.009 cm^{-1}) shows that the precision obtained is better than our Doppler limited resolution, so these constants were kept fixed in the $3s, 3d$ -complex treatment. To fix the absolute energy of all H₂ triplet states involved in our work we used the accurate determination of the energy difference $T_0 = 95\,076.446 \pm 0.005 \text{ cm}^{-1}$ between the ground state $X^1\Sigma_g^+ (v''=0, J''=0)$ and the lowest bound triplet state $a^3\Sigma_g^+ (v'=0, J'=0)$ ²³ of H₂ obtained by means of the anticrossing spectroscopic measurements of Miller and Freund.²⁴ As a result for the $c^3\Pi_u^-$ state, the energy levels, determined by fitting the infrared a - c transitions have a precision of 0.015 cm^{-1} . The adjustable parameters of the model were determined by least-squares fit to the spectroscopic energy levels for $v=0-3$, one v at a time. Two separate fits were made, one for each parity and the standard deviations between observed and calculated energy levels are of 0.03 cm^{-1} for the $-$ parity and 0.04 cm^{-1} for the $+$ parity. These are calculated assuming a normal statistical distribution of deviations. The correlation coefficient matrix indicates that the parameters of the model are rather independent. We must point out that line position measurements, obtained by a peak-finding procedure, have a precision better than 0.03 cm^{-1} . The unresolved fine and hyperfine structures broaden the rotational shapes in the case of H₂ $3s, 3d$ -triplet complex. So, the precision obtained in our fitting procedure reflects the rotational linewidth. The coupling parameters $W_1^{\Delta,11}$ and $W_1^{11\Sigma}$ are most strongly correlated to the centrifugal parameters D of the corresponding

states, but these correlations are weaker than the correlation between B and D parameters of the same state. The values of T_v , B_v , and D_v and the coupling parameters of the different electronic states are given in Table VII. The diagonal parameters for each state were obtained by fitting both the $-$ parity levels and the $+$ ones separately. The final diagonal values obtained for the two parities are found to be identical in the precision of their standard deviation. This result is in good agreement with the prediction that the diagonal parameters must be the same if, of course, the theoretical and experimental data are correct. Thus, the difference between the two parities results in the off-diagonal coupling parameters which clearly need not be the same. The $W_1^{\Delta,11}$ coupling parameter should be different for the two parities because it takes into account effects of interactions, which are especially important for the highly perturbed $+$ parity levels, with more highly excited states. Such interactions are not included specifically in the present form of the theory, so that in a sense what one actually obtains are effective constants. Furthermore, we can include the factor $(1-\delta)$ to account for any deviation in L from its free precession value of 0 or 2, but the model is already very flexible and this factor is taken into account implicitly in the $W_1^{\Delta,11}$ parameters. Due to the lack of observed high- J rotational transitions, the D_v and $W_2^{\Delta,11}$ parameters were determined through a special treatment. During the least-square-fit procedure the D_v and $W_2^{\Delta,11}$ parameters were fixed to a chosen value. Different values between 0 and 0.025 cm^{-1} were tried until the minimum standard deviation was obtained. The values, corresponding to the minimum standard deviation, are 0.018 cm^{-1} for both D_v and $W_2^{\Delta,11}$. This result is not surprising if we compare the B_v and $W_1^{\Delta,11}$ values which are of the same order of magnitude. The perturbation element between the $3s$ and $3d^3\Sigma_g^+$

TABLE VI. The molecular constants of the $c(2p)^3\Pi_u^-$ state.^a

V	T_v	B_v	D_v
0	94 881.93(5)	30.319(6)	0.0186(3)
1	97 223.60(3)	28.932(5)	0.0184(2)
2	99 443.21(2)	27.557(7)	0.0179(1)
3	101 540.76(1)	26.182(3)	0.0171(4)

^a All units are cm^{-1} . The number in parentheses corresponds to one standard deviation expressed in terms of the last digit. The standard deviation is 0.009 cm^{-1} and corresponds to the fit of the $2a-2c$ system of H₂ (see text).

TABLE VII. The *L*-uncoupled parameters for the 3*s*,3*d* complex of H₂.^a

	<i>T</i>	<i>B</i>	$W_{\uparrow}^{\wedge\wedge'}$ - parity	$W_{\uparrow}^{\wedge\wedge'}$ + parity	<i>E_z</i> ^b
Δ	112 354.06(2)	29.21(2)	28.52(2)	28.73(3)	75.0
Π	111 890.01(5)	28.35(5)			
Σ <i>d</i>	111 688.23(3)	27.38(3)	27.79(1)	27.88(5)	
Σ <i>s</i>	111 855.32(1)	30.12(4)			
<i>v</i> = 1					
Δ	114 565.07(1)	27.38(3)	27.06(6)	27.15(4)	85.0
Π	114 010.88(4)	26.80(3)			
Σ <i>d</i>	113 751.20(5)	25.75(1)	26.31(1)	26.38(3)	
Σ <i>s</i>	114 147.18(5)	28.79(6)			
<i>v</i> = 2					
Δ	116 656.15(7)	25.75(3)	24.42(5)	24.56(2)	95.0
Π	115 987.11(4)	25.50(1)			
Σ <i>d</i>	115 656.26(9)	24.38(1)	23.72(3)	23.80(1)	
Σ <i>s</i>	116 246.32(5)	27.30(8)			
<i>v</i> = 3					
Δ	118 613.08(7)	24.12(3)	23.32(4)	23.38(7)	105.0
Π	117 811.99(4)	23.85(1)			
Σ <i>d</i>	117 369.28(3)	22.90(7)	23.08(5)	22.93(2)	
Σ <i>s</i>	118 144.64(2)	25.80(8)			
St. Dev.			0.03	0.04	

^a All units are cm⁻¹. The number in parentheses corresponds to one standard deviation expressed in terms of the last digit.

^b Held fixed during the fit.

TABLE VIII. Calculated term value for the + parity levels (cm⁻¹).

<i>N</i>	<i>j</i> (3 <i>d</i>) ³ Δ _{<i>g</i>}	<i>o-c</i>	<i>i</i> (3 <i>d</i>) ³ Π _{<i>g</i>}	<i>o-c</i>	<i>g</i> (3 <i>d</i>) ³ Σ _{<i>g</i>}	<i>o-c</i>	<i>h</i> (3 <i>s</i>) ³ Σ _{<i>g</i>}	<i>o-c</i>
<i>v</i> = 0								
0					111 783.03	0.03	111 933.49	0.03
1			112 153.71	0.07	111 796.67	0.06	111 948.30	-0.05
2	112 529.66	0.05	112 311.08	0.02	111 826.70	-0.04	112 050.18	0.07
3	112 779.54	-0.03	112 503.79	0.04	111 896.79	0.02	112 223.36	0.03
4	113 093.05	0.04	112 741.09	-0.03	112 017.35	-0.03	112 457.84	-0.05
5	113 460.58	0.07	113 027.07	-0.05	112 190.93	0.05	112 748.99	0.04
<i>v</i> = 1								
0					113 883.31	0.04	114 178.81	-0.03
1			114 269.15	0.04	113 883.88	-0.05	114 198.13	0.04
2	114 712.18	0.03	114 419.48	0.07	113 911.05	-0.03	114 312.10	0.05
3	114 924.70	0.04	114 614.22	0.02	113 980.48	0.06	114 482.32	0.04
4	115 201.13	0.05	114 850.24	-0.05	114 097.45	0.02	114 707.13	-0.03
5	115 533.39	-0.03	115 129.15	-0.03	114 263.91	0.04	114 984.53	0.07
<i>v</i> = 2								
0					115 784.97	0.04	116 284.06	-0.06
1			116 182.28	-0.05	115 794.64	0.07	116 338.98	0.05
2	116 778.03	0.04	116 319.29	0.06	115 829.39	0.08	116 448.39	0.07
3	116 962.18	0.05	116 504.17	-0.02	115 902.05	-0.03	116 612.06	-0.04
4	117 203.99	-0.03	116 731.49	0.05	116 017.60	-0.05	116 827.15	-0.03
5	117 498.64	-0.07	116 999.81	0.04	116 178.46	-0.03	117 093.62	-0.03
<i>v</i> = 3								
0					117 508.84	0.04	118 271.10	-0.03
1			117 983.74	-0.04	117 527.44	0.05	118 323.81	0.05
2	118 725.69	0.04	118 106.95	-0.05	117 571.48	0.08	118 428.79	0.03
3	118 887.74	0.06	118 278.96	-0.03	117 649.55	-0.02	118 585.19	0.06
4	119 100.05	-0.05	118 484.75	-0.033	117 766.02	0.04		
5	119 364.54	0.03	118 731.49	0.04	117 923.40	0.03		

TABLE IX. Calculated term value for the - parity levels (cm⁻¹).

<i>N</i>	<i>j</i> (3 <i>d</i>) ³ Δ _{<i>g</i>}	<i>o-c</i>	<i>i</i> (3 <i>d</i>) ³ Π _{<i>g</i>}	<i>o-c</i>
<i>v</i> = 0				
1			112 066.93	0.03
2	112 514.26	0.02	112 141.14	0.05
3	112 732.72	0.05	112 265.53	0.02
4	113 008.29	0.04	112 442.47	-0.04
5	113 335.79	-0.02	112 668.64	-0.03
6	113 706.68	-0.03	112 930.01	-0.02
<i>v</i> = 1				
1			114 177.98	-0.02
2	114 706.34	0.03	114 259.33	-0.03
3	114 901.73	0.02	114 384.75	0.03
4	115 154.64	-0.07	114 557.08	0.04
5	115 463.02	0.03	114 777.29	0.05
<i>v</i> = 2				
1			116 144.79	0.03
2	116 776.39	0.04	116 226.98	0.05
3	116 956.88	-0.05	116 352.34	0.02
4	117 183.54	-0.03	116 522.41	-0.07
5	117 467.37	0.03	116 738.18	-0.02
<i>v</i> = 3				
1			117 961.02	0.04
2	118 722.04	-0.06	118 042.95	0.03
3	118 884.57	-0.05	118 167.44	0.02
4	119 095.16	0.02	118 339.72	-0.05
5	119 339.44	0.02	118 542.12	0.03

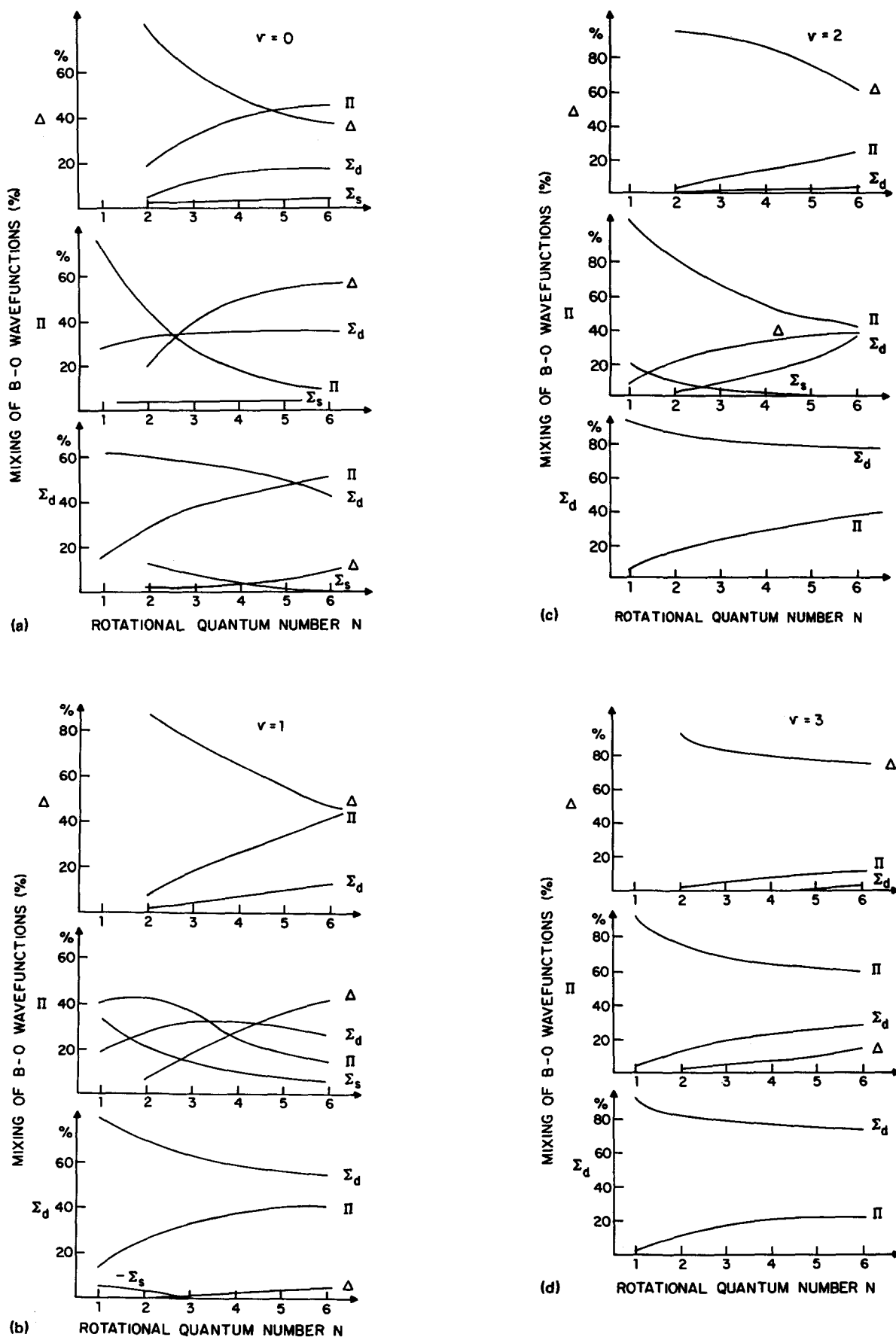


FIG. 3. (a) Mixing of the + parity Born-Oppenheimer wave functions for the 3d-triplet complex of states. The squared coefficients of the individual pure state are plotted vs N for $v = 0$. (b) Squared coefficients of the individual pure state are plotted vs N for $v = 1$. (c) Squared coefficients of the individual pure state are plotted vs N for $v = 2$. (d) Squared coefficients of the individual pure state are plotted vs N for $v = 3$.

states was taken from the work of Wakefield and Davidson⁸ for $v = 0, 1$ and was extrapolated for $v = 2, 3$, assuming that E_{Σ} varies linearly with $(v \pm 1/2)$. The coupling parameters $W_1^{\Delta, 11}$ and $W_1^{\Pi, 2}$ decrease significantly when the vibrational quantum number increases. These parameters represent the interaction between the neighboring vibrational levels. The vibrational levels are coupled together as it is shown by Zare *et al.*²² and Mizushima.²⁵ Briefly, the contribution of the other vibrational states can be expressed as

$$\sum_{v' \neq v} \frac{\langle nv | B(R) | nv' \rangle \langle nv' | B(R) | nv \rangle}{E_{nv} - E_{nv'}}$$

So when we consider each vibrational level separately, for increasing vibrational quantum number, the positive contribution of the other upper vibrational levels is smaller while the contribution of the lower vibrational levels becomes negative. Previous work on the L -uncoupling in H₂ (Refs. 12 and 13) did not show such a reduction of the coupling parameters $W_1^{\Lambda, \Lambda'}$ and used the approximation:

$$W_1^{\Lambda, \Lambda'} = (B_{\Lambda} + B_{\Lambda'})/2$$

which leads to a good but not complete representation of the observed energy levels. Keiding and Bjerre,¹⁵ in their recent work on the $3d$ complex of HD, show such a decrease but in their explanation, they omitted the effect of the neighboring vibrational levels.

The calculated term values and differences with the experimental ones are collected in Tables VIII–IX. The highest levels observed are 119 364.54, 119 084.72, 118 731.49, and 118 585.19 cm⁻¹ which correspond to the $j(v' = 3, J' = 5)$, $g(v' = 4, J' = 1)$, $i(v' = 3, J' = 5)$, and $h(v' = 3, J' = 4) +$ parity states, respectively. The level corresponding to the g state was simply evaluated by using the $(v'' = 4, J'' = 1)$ level position of the lower state given by Dieke²⁶ and corrected²⁴ by -149.56 cm⁻¹, and the observed $Q 1(4,4)$ line attributed to the g - c system. All these levels lie above the H(1s)–H(2l) dissociation limit (118 375.6 cm⁻¹). The closeness between the j and g potential curves and the difference between their observed two highest levels suggest the existence of other close lying levels in the g state, but not observed because they predissociate. De Bruijn and Helm,²⁷ very recently, observed high vibrational levels (up to $v = 9$) attributed to the j, i and h states by fast photofragment laser spectroscopy extended to the neutral molecules. Also, as a result of this work, we have been able to correct some misassignments in Dieke's table²⁶ for the $P 1 v = 0$ and $v = 1$ lines of the g state and for the $P 1, P 2$ and $Q 1 v = 0$ and $P 1 v = 1$ lines of the h state.

The eigenvectors provide good insight into the nature of the $3d$ -complex. The mixing calculated from the eigenvectors of the $+$ parity levels is illustrated in Fig. 3 For $v = 0$, where the mixing is the strongest, each state can no longer be classified according to its Λ character alone. In all cases, the L -uncoupling increases with the rotational quantum number N . Figure 3 also provides a rather clear picture of the participation of the $h(3s)^3\Sigma_g^+$ state in the $3d$ -complex. There is quite a strong participation of this state for the lowest rotational levels of the $g(3s)^3\Sigma_g^+$ state in its $v = 0$ level. However, this participation falls rapidly for higher N and,

for a given N , decreases for higher v . We note also a strong participation of the $h(3s)^3\Sigma_g^+$ basis state in the $i(3d)^3\Pi_g^+$ final state for low N values, particularly for $v = 1$. There is some tendency for the participation to decrease for higher N but this tendency is not really as pronounced as for the $g(3d)^3\Sigma_g^+$ state. Finally, the direct participation of the $h(3s)^3\Sigma_g^+$ basis state in the $j(3d)^3\Delta_g^+$ final state is quite small for $v = 0$ and absent for $v \neq 0$. In conclusion, it is found necessary to include interactions with the $h(3s)^3\Sigma_g^+$ state to describe adequately the lower v and N energy levels of the $3d$ -triplet complex of states.

V. CONCLUSION

A low pressure discharge has allowed us to record, with a Fourier transform spectrometer, the $3s, 3d \rightarrow 2p$ transitions of the H₂ molecule. The clarity of the spectra led to a new set of data used as an input for an L -uncoupling model which simulates the electrostatic interactions and the rotational breakdown of the Born–Oppenheimer approximation in the $3s, 3d$ -complex. Note that the multichannel quantum-defect theory (MQDT)²⁸ could also be a convenient method for the treatment of the $3s, 3d$ -triplet complex of states. This method was used several times in recent years to a broad range of problems in atomic and molecular physics^{29,30} especially for the description of highly excited states of neutral systems. Presently, calculations are in progress on the g factors following the previous experimental work of Jost *et al.*¹³ in their analysis of the Zeeman effect in the $3s, 3d$ -triplet complex. We think it will be a good test of the accuracy of the eigenvectors resulting from our approach to the analysis of the $3s, 3d$ -triplet complex of states of H₂.

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