

Band Spectra and Hyperfine Structure of HgH, HgD, and HgT¹

DAVID M. EAKIN² AND SUMNER P. DAVIS

Department of Physics, University of California, Berkeley, California 94720

The analysis of the band spectrum ($A_1^2 \Pi_{1/2}-X^2\Sigma^+$ system) of HgH has been extended to include $v'' = 4$, and that of HgD to include $v'' = 5$. Rotational constants for these levels have been calculated. The HgT molecular spectrum has been produced, partially analyzed, and some constants have been calculated. Spin splitting in the ground state of all three molecules is discussed and vibrational energy levels are compared. Magnetic hyperfine structure in the band spectra of ¹⁹⁹HgD and ¹⁹⁹HgT has been observed and analyzed. Measurements are presented and the analysis is compared with theory.

INTRODUCTION

This work, briefly reported earlier (1), is a continuation of the work on HgH by Porter (2) for the Berkeley Analyses of Molecular Spectra program (3). We have investigated certain bands in the spectra of HgH and HgD which are particularly valuable for determining the shape of the ground state potential energy curve near the dissociation limit. We have also analyzed a portion of the HgT spectrum; this constitutes the first reported observation of this molecule.

The spacing of the vibrational levels in the different isotopic forms of the molecule changes approximately by the factor $\rho = (\mu/\mu')^{1/2}$, where $\mu = m_1m_2/(m_1 + m_2)$, the reduced mass of the molecule. The HgH-D-T spectra make an interesting picture (see Fig. 1) as the isotope shifts are nearly the largest possible for a diatomic molecule, ρ being 0.7091 for H-D and 0.5809 for H-T. (Adding neutrons to the mercury nucleus instead of to the hydrogen nucleus shifts the positions of the levels about four orders of magnitude less) (4). Vibrational energy levels of HgH, HgD, and HgT are compared in Fig. 2.

The magnetic hyperfine structure of HgD and HgT was investigated to confirm or elucidate some points of interpretation in the study of hyperfine structure in HgH by Porter and Davis (5).

¹ This work was supported in part by a grant from the National Science Foundation.

² Present address: Science Department, John Swett High School, Crockett, California 94525.

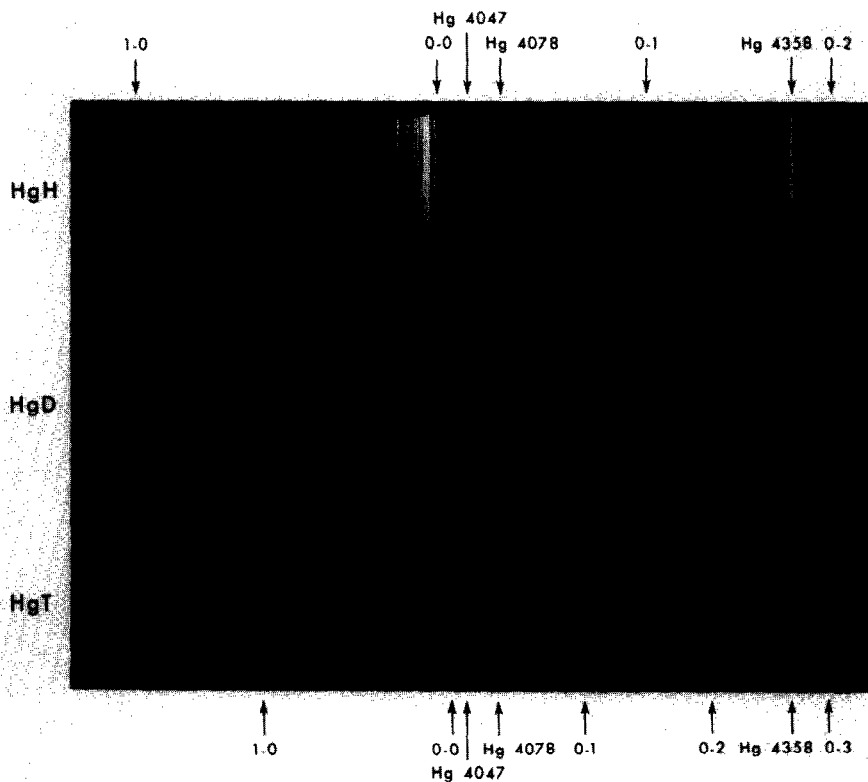


Fig. 1. Bands in the $A_1 \ ^2\Pi_{1/2}-X \ ^2\Sigma^+$ system, showing vibrational isotope shift.

EXPERIMENTAL METHODS

The spectra were produced by electrodeless discharge tubes containing mercury in an atmosphere of argon and hydrogen. Natural mercury was used for the rotational analysis part of the work; for the hyperfine structure studies, an enriched isotope (83% ^{199}Hg) was obtained from the Oak Ridge National Laboratory. The tritium (^3H) was also obtained from ORNL and was about 98% pure, with ^1H the principal impurity. The HgT discharge tubes contained 75 mci of the gas, which presented no radiation hazard so long as the gas was confined to the tube.

The molecular spectra were photographed on Kodak 103a-O plates with interferometrically measured thorium lines (β) as wavelength standards. Exposures were made with a 6.4-m concave grating (Paschen-Runge mounting) and a Czerny-Turner plane grating with 3-m focal length mirrors. For the hyperfine structure observations, a Fabry-Perot interferometer was used with 15 and 17-mm spacers; cross-dispersion was provided by the plane grating spectrograph.

The plates were measured on a semiautomatic photoelectric comparator with punched card output. The wavelength calculations were performed by the CDC

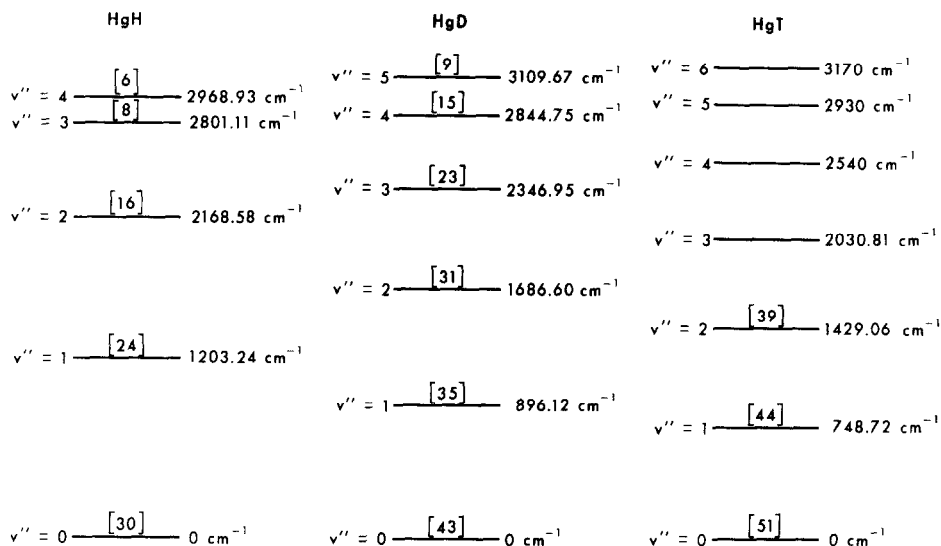


FIG. 2. Vibrational energy levels in the ground state, $^2\Sigma^+$. Here the lowest vibrational level for each molecule is arbitrarily set equal to zero. If zero is set at the true bottom of the potential well instead, then 672.33 cm^{-1} is to be added to all HgH energies, 485.20 cm^{-1} to all HgD energies, and 393.41 cm^{-1} to HgT energies. (These zero-point energies were calculated from the spectroscopic constants, a procedure of dubious accuracy for such an anharmonic potential. The problem of the potential energy curve for these molecules has been studied most recently by Stwalley (9). His detailed theoretical treatment, Chap. 7 of Ref. (9a), gives a zero-point energy of 683.1 cm^{-1} for HgH.) In brackets are the maximum values of the rotational quantum number for each vibrational level.

6400 at the Berkeley Computer Center. Most of the results reported here are averages of several sets of measurements. Complete details of the experimental procedures are available elsewhere (7).

ROTATIONAL ANALYSIS AND MOLECULAR CONSTANTS

The ground state ($X^2\Sigma^+$) of HgH predissociates at a very low energy and few vibrational levels exist. The first four ($v'' = 0, 1, 2, 3$) have been thoroughly studied. The $v'' = 4$ level was observed by Hulthén (8) but his measurements were not confirmed by later investigators due to the extreme faintness of transitions to this level. With modern facilities we have been able to resolve some lines he reported blended and to improve the accuracy of his measurements on the 0-4 band of the A_1-X system. The complete analysis is given in Table I.

Accurate knowledge of the HgH potential has recently been needed in connection with experiments on scattering of H atoms by Hg (9). Since the $v'' = 4$ level lies very close to the dissociation limit and is therefore of great importance in determining the shape of the potential curve in that region, the actual rotational

TABLE I
 ROTATIONAL ANALYSIS OF THE HgH 0-4 BAND, $A_1^2\Pi_{1/2}-X^2\Sigma^+$ SYSTEM^a

Lambda	Int	Sigma	P_{12}	P_1	Q_{12}	Q_1	R_{12}	R_1
4551.981	2	21 962.30	2					
4551.518	10 ^b	21 964.53		1				
4551.511	10 ^b	21 964.60			1			
4550.227	4	21 970.76				0		
4549.259	3	21 975.44	3					
4548.979	10 ^b	21 976.80		2				
4548.945	10 ^b	21 976.96			2			
4547.200	1	21 985.39						0
4546.407	10 ^b	21 989.23				1		
4546.391	10 ^b	21 989.30					1	
4544.316	6	21 999.35	4					
4544.242	8 ^b	21 999.70		3				
4544.201	10 ^b	21 999.90			3			
4541.365	2	22 013.64						1
4540.476	9 ^b	22 017.95				2		
4540.441	6 ^b	22 018.12					2	
4537.316	2	22 033.28		4				
4537.267	10	22 033.52			4			
4537.072	4	22 034.47	5					
4533.440	4	22 052.12						2
4532.392	10 ^b	22 057.22				3		
4532.345	8 ^b	22 057.45					3	
4528.105	5	22 078.10		5				
4528.052	9	22 078.36			5			
4527.396	4	22 081.56	6					
4523.389	5	22 101.12						3
4522.141	8	22 107.22				4		
4522.084	3	22 107.50					4	
4516.463	10 ^c	22 135.00		6				
4516.410	8	22 135.27			6			
4511.191	5	22 160.88						4
4509.668	7	22 168.36				5		
4509.619	3	22 168.60					5	
4496.792	2	22 231.84						5
4494.818	4	22 241.60				6		
4494.778	1	22 241.80					6	
4480.064	1	22 314.85						6

^a Lambda is the wavelength in Å in standard air. Int is the approximate line intensity on an arbitrary scale of 10 (^b a blend with another line of the same band; and ^c a blend with a line of the 0-3 band). Sigma is the wavenumber (cm^{-1}) in vacuum, P_{12} to R_1 is the value of the rotational quantum number K'' for the ground state level involved in the transition. Predissociation occurs for K'' greater than 6.

TABLE II
HgH ROTATIONAL ENERGY LEVELS FOR $v'' = 4$ OF $X^2\Sigma^+$ ^a

K	J	Parity	Relative energy	Total energy	Spin splitting	Gamma
0	0.5	+	0.	2968.93	0.	—
1	0.5	—	2.81	2971.74		
1	1.5	—	2.88	2971.81	0.07	0.047
2	1.5	+	8.45	2977.38		
2	2.5	+	8.62	2977.55	0.17	0.068
3	2.5	—	16.67	2985.60		
3	3.5	—	16.89	2985.82	0.22	0.063
4	3.5	+	27.22	2996.15		
4	4.5	+	27.48	2996.41	0.26	0.058
5	4.5	—	39.69	3008.62		
5	5.5	—	39.95	3008.88	0.26	0.047
6	5.5	+	53.12	3022.05		
6	6.5	+	53.30	3022.23	0.18	0.028

^a Total energy is measured from $K'' = 0$ in the lowest vibrational level, not from the bottom of the potential well (see Fig. 3). Gamma is the spin-splitting coefficient.

energies are given in Table II to supplement the energy level tables of HgH made by Porter (10). There are a few faint lines to the red of the 0–4 band, but they do not seem to form a regular band structure, so there is no spectroscopic evidence for a vibrational level higher than $v'' = 4$ in the ground state.

For $v'' = 4$ of HgH, the rotational levels from $K'' = 2$ to $K'' = 4$ can be fitted well with the following constants: $B'' = 1.451 \pm 0.001 \text{ cm}^{-1}$ and $D'' = 4.07 \pm 0.03 \times 10^{-3} \text{ cm}^{-1}$. The highest levels ($K'' = 5$ and 6) cannot be fitted, even with the addition of higher order constants in the expansion. The spacings of the higher vibrational and rotational levels change very rapidly in the ground state of HgH; thus “constants” are less useful and meaningful than usual and should be used only with caution and awareness of how they were calculated. See for example the treatment of the constants by Fujioka and Tanaka (11) and Porter (10). Hulthén’s constants ($B'' = 1.473$ and $D'' = 4.75 \times 10^{-3}$) give an “average fit” to all six levels.

The spin-splitting constant is very inconstant. It decreases rapidly as the amount of vibration or rotation increases, and also as the mass of the Hg partner increases. Furthermore its rate of change with K'' and v'' also varies with isotopic mass. The theory of spin splitting in $^2\Sigma$ states developed by Van Vleck (12) shows that γ is dependent on K'' and v'' in approximately the same way as the rotational constant B'' is, at least in the case of HgH (7), and thus may be represented by a power series expansion, as was later found empirically by Fujioka and Tanaka (11). The value of the constant at $K'' = 0$ is given in Table III. The isotope ratios of γ_0 (HgD/HgH, HgT/HgH, and HgT/HgD) are 0.508,

TABLE III
THE SPIN-SPLITTING COEFFICIENT γ (cm⁻¹) AT $K'' = 0$ FOR $X^2\Sigma^+$ ^a

v''	HgH (cm ⁻¹)	HgD (cm ⁻¹)	HgT (cm ⁻¹)
0	2.134 ± 0.003	1.085 ± 0.002	0.744 ± 0.003
1	1.770 ± 0.003	0.979 ± 0.002	0.681 ± 0.003
2	1.330 ± 0.005	0.839 ± 0.004	0.607 ± 0.002
3	0.660 ± 0.005	0.672 ± 0.004	0.530 ± 0.003
4	0.071 ± 0.002	0.482 ± 0.009	—
5	—	0.145 ± 0.005	—
6	—	—	—

^a All HgH values are from Porter (10) except γ_4 which is from this work. All HgD values are from Fujioka and Tanaka (11) except γ_6 (this work). All HgT values are from this work.

0.349, and 0.686, reasonably close to $\rho^2 = 0.503, 0.337,$ and $0.671,$ respectively, as would be expected from Van Vleck's theory.

HgD

Much of the HgD spectrum was analyzed by Fujioka and Tanaka (11), but we have extended their analysis, adding faint lines at the heads and tails of bands and resolving some lines earlier reported blended. These improved tables of rotational analysis are available at the Berkeley Spectroscopy Laboratory and will not be reproduced here. The bands we have reworked are the 0-0, 0-1, 0-2, 0-3, and 0-4 in the A_1-X system and the 0-2 and 0-3 in the A_2-X system. In addition, some new bands of the A_1-X system have been analyzed: 1-2, 2-2, 1-0, and 0-5. The 0-5 band involves the highest vibrational level that exists in the ground state; therefore the complete analysis of this band is given (Table IV) as well as the rotational energy levels out to the point of dissociation (Table V). The $v'' = 5$ rotational levels from $K'' = 3$ through $K'' = 8$ can be fitted with the following constants: $B'' = 1.1729$ cm⁻¹, $D'' = 1.627 \times 10^{-3}$ cm⁻¹, and $H'' = -3.00 \times 10^{-6}$ cm⁻¹. The sign of H'' is chosen to follow the formulas of Herzberg (13).

HgT

The HgT spectrum has been analyzed only as far as necessary to carry out the hyperfine structure studies. The bands analyzed are listed in Table VI. Rotational constants for the lowest four vibrational levels of the ground state are given in Table VII. Transitions to the highest three vibrational levels are much fainter (see Fig. 3) and have not yet been analyzed. The spin-splitting constants are given in Table III. Because of the anharmonicity of the molecule, the equilibrium rotational constants were calculated using only the lowest three vibrational levels, as was done by Fujioka and Tanaka (11) for HgH and HgD.

The vibrational constants for the ground state ($X^2\Sigma^+$) are: $\omega_e'' = 803.48$ cm⁻¹, $x\omega_e'' = 26.53$ cm⁻¹, and $y\omega_e'' = -1.702$ cm⁻¹. These were determined from the $\Delta G_{v+1/2}''$ values of 748.72, 680.34, and 601.75 cm⁻¹, respectively.

TABLE IV
 ROTATIONAL ANALYSIS OF THE HgD 0-5 BAND, $A_1^2\Pi_{1/2}-X^2\Sigma^+$ SYSTEM^a

Lambda	Int	Sigma	P_{12}	P_1	Q_{12}	Q_1	R_{12}	R_1
4602.206	2	21 722.63	2					
4601.639	3 ^b	21 725.30		1				
4601.607	3 ^b	21 725.45			1			
4601.353	3	21 726.65	3					
4600.778	2	21 729.37				0		
4600.714	3	21 729.67		2				
4600.642	4	21 730.01			2			
4599.544	3	21 735.20	4					
4599.216	3	21 736.75						0
4598.987	4 ^b	21 737.83				1		
4598.972	4 ^b	21 737.90					1	
4598.843	3	21 738.51		3				
4598.748	5	21 738.96			3			
4596.742	3	21 748.44	5					
4596.388	3	21 750.12						1
4596.299	6 ^b	21 750.55				2		
4596.278	6 ^b	21 750.65					2	
4596.020	4	21 751.86		4				
4595.902	5	21 752.42			4			
4592.904	4	21 766.62	6					
4592.664	10 ^b	21 767.75				3		
4592.664	10 ^b	21 767.75						2
4592.582	3	21 768.14					3	
4592.197	4	21 769.97		5				
4592.064	6	21 770.60			5			
4588.092	5	21 789.45				4		
4587.992	6 ^b	21 789.92					4	
4587.992	6 ^b	21 789.92						2
4587.965	4 ^b	21 790.05	7					
4587.324	3	21 793.10		6				
4587.199	4	21 793.69			6			
4582.533	5	21 815.88				5		
4582.403	4 ^b	21 816.50					5	
4582.403	4 ^b	21 816.50						4
4581.865	2	21 819.06	8					
4581.357	2	21 821.48		7				
4581.242	4	21 822.03			7			
4575.955	5	21 847.24				6		

TABLE IV—*Continued*

Lambda	Int	Sigma	P_{12}	P_1	Q_{12}	Q_1	R_{12}	R_1
4575.823	4 ^b	21 847.87					6	
4575.823	4 ^b	21 847.87						5
4574.502	1	21 854.18	9					
4574.223	1	21 855.51		8				
4574.121	3	21 856.00			8			
4568.290	4	21 883.90				7		
4568.231	3 ^b	21 884.18						6
4568.195	3 ^b	21 884.35					7	
4565.838	1	21 895.65		9				
4565.764	2	21 896.00			9			
4559.570	2	21 925.75						7
4559.486	3	21 926.15				8		
4559.370	1	21 926.71					8	
4549.780	2	21 972.93						8
4549.444	2	21 974.55				9		
4549.371	2	21 974.90					9	
4538.767	1	22 026.24						9

* The symbols are the same as in Table I. Predissociation occurs for K'' greater than 9.

HYPERFINE STRUCTURE

Number of Components. ¹⁹⁹Hg has a nuclear spin of $\frac{1}{2}$ and a magnetic moment of $+0.50413$ nuclear magnetons. Since magnetic hyperfine splitting occurs in both the upper and lower electronic states, lines in the spectra of HgH, HgD, and HgT should have four components. This should be true for Q branches, but the selection rule $\Delta F = 0, \pm 1$ reduces the number of possible components to three for P and R branches, where $\Delta J = \pm 1$. However, only two components are observed in lines of ¹⁹⁹HgH, ¹⁹⁹HgD, and ¹⁹⁹HgT. To explain this, Porter and Davis (4) (hereafter referred to as paper I) postulated that transitions with $\Delta F \neq \Delta J$ are either forbidden or suppressed. The theoretical explanation is available in the matrix elements for the transitions. These have been calculated up to $J = 10$ by Townes and Schawlow (14). Their tables show that the two transitions given by $\Delta F = \Delta J$ account for almost all of the intensity, while transitions given by $\Delta F \neq \Delta J$ have a negligible fraction of the total intensity (except at extremely low J values, where they have a few percent of the total, with a maximum of 11% for $J = 1$).

Intensity of Components. For HgD and HgT, as with HgH, the two components of each line generally have equal intensities, but near band heads differences become apparent. In all of the bands investigated, the long wavelength component is the stronger of the two in the R_1 , Q_1 , and P_1 branches, while the short wavelength component is stronger in the R_{12} , P_{12} , and Q_{12} branches. This intensity dif-

ference is quite pronounced at the band origin, but decreases very rapidly with increasing rotation.

Magnitude of Splittings. As in HgH, the magnitudes of the splittings in HgD and HgT are not the same in all branches. The splittings in the P and R branches are much larger than those in the Q branches, typical values being 0.13 and 0.06 cm^{-1} , respectively. This property holds for all bands of the A_1-X system. In the A_2-X system there is little if any difference between the various branches.

The splittings remain nearly constant with J except near the band origins, where the splittings become quite large (P_1 , R_1 , and Q_1 branches) or quite small (P_{12} , R_{12} , and Q_{12} branches). This behavior is well illustrated by Fig. 3 of paper I.

Effect of the Hydrogen Nucleus. The magnitude of the hyperfine splitting depends on $\langle 1/r^3 \rangle$, the average distance of the unpaired electrons from the nucleus, and on $\psi^2(0)$, the electron probability density at the position of the nucleus. In HgH, HgD, and HgT, both of these factors are much greater when evaluated with respect to the mercury nucleus than for the hydrogen nucleus. Therefore paper I assumed that the entire observed hyperfine splittings in HgH were caused by the magnetic moment of the mercury nucleus, with the magnetic moment of the hydrogen nucleus having negligible effect. This seems to be confirmed by the present investigation. Careful measurements have been made of the splittings in 416 lines in the 0-0, 0-1, and 0-2 bands of HgD (A_1-X system) and for 302 lines in the 0-0 and 0-1 bands of HgT (A_1-X system). They are very similar to those in HgH, both in magnitude and behavior, although the following differences are discernible. The splittings decrease with v'' more rapidly for HgH than they do for HgD or HgT. For example, the magnitudes of the HgH and HgD splittings are nearly identical in the 0-0 band, but in the 0-2 band they are much smaller in HgH than in HgD. Also, the splittings in the Q branches decrease rather markedly with J in HgH (see Fig. 3 of paper I); whereas, this behavior is either absent or is much less noticeable in HgD and HgT. These differences are due to the greater anharmonicity of the HgH molecule, as explained below, rather than the different magnetic moment of the hydrogen nucleus.

Energy Level Splittings. The energy level scheme developed in paper I to explain the observations on ^{199}HgH applies also to HgD and HgT. It is desirable to know the magnitudes of the hyperfine splittings in the energy levels, but the experimental observations give only the splittings in the spectral lines, which are either the sums (P and R branches) or the differences (Q branches) of the splittings in the upper and lower states. From combination differences alone it is not possible to obtain the absolute value of the splitting in any level because selection rules prohibit the necessary transitions. One may start therefore by assigning to any one level an arbitrary value for the hyperfine splitting and from this initial value a table of splittings in other rotational levels may be calculated using combination differences. This produces results for only half of the levels, because the operation of the parity selection rule limits transitions to those of a particular

TABLE V
 HgD ROTATIONAL ENERGY LEVELS FOR $v'' = 5$ OF $X^2\Sigma^+a$

K	J	Parity	Relative energy	Total energy	Spin splitting	Gamma
0	0.5	+	0.	3109.67	0.	—
1	0.5	—	2.23	3111.90		
1	1.5	—	2.37	3112.04	0.14	0.093
2	1.5	+	6.74	3116.41		
2	2.5	+	7.08	3116.75	0.34	0.136
3	2.5	—	13.55	3123.22		
3	3.5	—	13.98	3123.65	0.43	0.123
4	3.5	+	22.44	3132.11		
4	4.5	+	22.99	3132.66	0.55	0.122
5	4.5	—	33.26	3142.93		
5	5.5	—	33.89	3143.56	0.63	0.115
6	5.5	+	45.80	3155.47		
6	6.5	+	46.40	3156.07	0.60	0.093
7	6.5	—	59.69	3169.36		
7	7.5	—	60.25	3169.92	0.56	0.075
8	7.5	+	74.57	3184.24		
8	8.5	+	75.08	3184.75	0.51	0.060
9	8.5	—	89.99	3199.66		
9	9.5	—	90.34	3200.01	0.35	0.037

* The symbols are the same as in Table II.

system. To obtain values for the splittings in the other levels it is necessary to define arbitrarily the value of the splitting in some additional level. Having now built up a complete table of splittings it is desirable to remove the arbitrariness of the two initially chosen values. This may be done by utilizing the theoretical predictions as follows.

The hyperfine splittings in the $^2\Pi$ state, which is case a_{BJ} , are given by Townes and Schawlow (14) as,

$$\Delta E_{hfs} = \mathbf{I} \cdot \mathbf{J} [aA + (b + c)\Sigma] \frac{\Omega}{J(J+1)} \pm \mathbf{I} \cdot \mathbf{J} \left[\frac{d(\pm X + 2 - Y) \left(J + \frac{1}{2} \right)}{\pm 4XJ(J+1)} \right], \quad (1)$$

where the second term is due to the lambda-doubling. The $^2\Pi$ state of HgH is so strongly Hund's case a that A is very large (3684 cm^{-1}), giving $Y \approx 550$ and $X = [Y(Y-4) + 4(J + \frac{1}{2})^2]^{1/2} \approx Y$. For the $^2\Pi_{3/2}$ state ($+X$) the lambda-doubling term is therefore negligible and the two components of the lambda-doublet have the same splitting. The first term decreases approximately as $1/J$, so the splittings are very small except at the band origin, which explains the ob-

TABLE VI
BANDS ANALYZED IN THIS WORK^a

Molecule	Band	Lambda head (Å)	Sigma head (cm ⁻¹)	Intensity
<i>A</i> ₁ ² Π _{1/2} - <i>X</i> ² Σ ⁺ system				
HgH	0-4	4551.981	21 962.30	1
HgD	0-5	4602.206	21 722.63	1
	0-4	4547.574	21 983.58	2
	0-3	4447.535	22 478.05	10
	0-2	4321.155	23 135.46	20
	0-1	4179.336	23 920.50	50
	1-2	4075.180	24 531.87	15
	0-0	4029.397	24 810.60	100
	2-2	3864.149	25 871.58	5
	1-0	3815.040	26 204.61	40
HgT	0-3	4393.700	22 753.47	10
	0-2	4280.917	23 352.91	30
	0-1	4160.158	24 030.77	60
	0-0	4035.008	24 776.10	100
	1-0	3855.900	25 926.93	50
<i>A</i> ₂ ² Π _{3/2} - <i>X</i> ² Σ ⁺ system				
HgD	0-3	3821.176	26 162.53	8
	0-2	3727.572	26 819.49	15

^a All are degraded to the blue.

servation of approximately equal splittings for all *P*, *Q*, and *R* lines in the *A*₂-*X* system. For the ²Π_{1/2} state (*-X*) the lambda-doubling term is not negligible at all but becomes approximately,

$$\pm \mathbf{I} \cdot \mathbf{J} \left[\frac{d \left(J + \frac{1}{2} \right)}{2J(J+1)} \right],$$

so the total hyperfine splitting is ($\Lambda = 1$, $\Sigma = -\frac{1}{2}$, $\Omega = \frac{1}{2}$),

$$\Delta E_{hfs} = \frac{\mathbf{I} \cdot \mathbf{J}}{2J(J+1)} \left[a - \frac{b}{2} - \frac{c}{2} \pm d \left(J + \frac{1}{2} \right) \right], \quad (2)$$

and since $\mathbf{I} \cdot \mathbf{J} = \frac{1}{2}[F(F+1) - J(J+1) - I(I+1)]$ and $I = \frac{1}{2}$, the splitting between $F = J + \frac{1}{2}$ and $F = J - \frac{1}{2}$ is

$$\Delta E_{hfs} = \frac{J + \frac{1}{2}}{2J(J+1)} \left[a - \frac{b}{2} - \frac{c}{2} \pm d \left(J + \frac{1}{2} \right) \right]. \quad (3)$$

For large *J* this becomes approximately $\Delta E = \pm d/2$, that is, the splittings in the

TABLE VII
 ROTATIONAL CONSTANTS FOR THE GROUND STATE OF HgT, $X^2\Sigma^+$ ^a

v''	B'' (cm ⁻¹)	$D'' \times 10^5$ (cm ⁻¹)	$H'' \times 10^9$ (cm ⁻¹)
0	1.8464	4.111	-2.72
1	1.7691	4.795	0.57
2	1.6806	5.586	-2.47
3	1.5757	7.957	16.6

(cm ⁻¹)	(cm ⁻¹)
$B_e = 1.8808$	$D_e = 3.769 \times 10^{-5}$
$\alpha_e = 0.0661$	$\beta_e = 0.684 \times 10^{-5}$
$\gamma_e = -0.0056$	

^a The sign of H follows Herzberg (13).

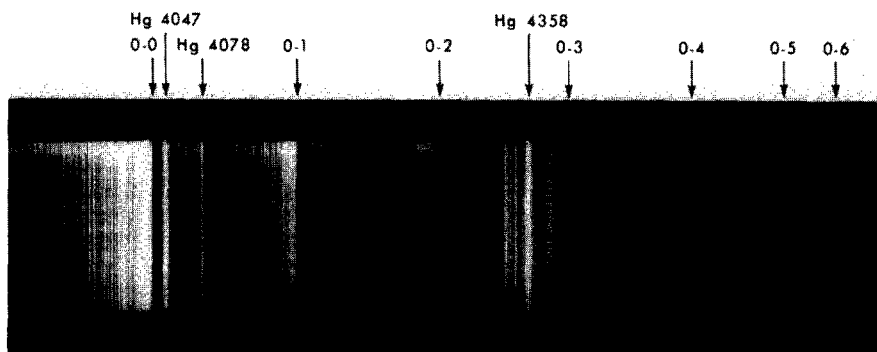


FIG. 3. v'' progression in the A_1-X system of HgT.

two components of the lambda-doublet are equal but in opposite directions, the upper one being regular and the lower one inverted. Furthermore, for large J the splittings are nearly independent of J , which agrees with the experimental result shown by the table of level splittings calculated from combination differences. The fact that the two components have equal splittings makes it possible now to eliminate one of the initially arbitrary values: one value is adjusted so that the two components have equal splittings at large J .

Turning now to the ground state, $^2\Sigma$ (coupling case $b_{\beta J}$), the equations of Townes and Schawlow for the splittings reduce to

$$\left. \begin{aligned} \Delta E_{hfs} &= \frac{I \cdot J}{2K + 1} \left[b + \frac{c}{2K + 3} \right] & \text{for } J = K + \frac{1}{2} \\ \Delta E_{hfs} &= \frac{I \cdot J}{2K + 1} \left[-b + \frac{c}{2K - 1} \right] & \text{for } J = K - \frac{1}{2} \end{aligned} \right\} \quad (4)$$

Evaluating $\mathbf{I} \cdot \mathbf{J}$ we obtain the hyperfine splittings

$$\frac{K+1}{2K+1} \left[b + \frac{c}{2K+3} \right] \quad \text{and} \quad \frac{K}{2K+1} \left[-b + \frac{c}{2K+1} \right]$$

for the upper and lower components of the spin doublet, respectively. For large K these become $+b/2$ and $-b/2$, a result similar to that in the ${}^2\Pi_{1/2}$ state: the splittings in the two components of the doublet are equal and constant. (Paper I made the confusing statement that the theory predicted the splittings neither to remain constant nor to decrease, but to undergo an intermediate behavior.) A second important result is that the splittings in the two components are in opposite directions, again similar to the situation in the ${}^2\Pi_{1/2}$ state: the upper one is regular while the lower one is inverted. Thus the inversion in the ${}^2\Sigma$ state, assumed in paper I, is in full agreement with the theory.

Now the one remaining arbitrariness in the table of level splittings can be removed. The splittings in the two components of the spin doublet in the ground state are the same, and the initial value may be fitted to this condition. (Alternatively one may make use of the observations that for large J the splittings in lines of the Q_1 and Q_{12} branches, or the P or R branches, are the same. Either argument gives the same result.) Thus from a table of relative splittings in the levels, a complete table of the absolute splittings in all levels is obtained. The results for the 0-1 band of HgD are given as an example in Fig. 4 and 5.

Correspondence with Theory. As is shown in Fig. 4, the splittings in the two components of the lambda-doublet in the ${}^2\Pi_{1/2}$ state are essentially the same for large J , about 0.357 cm^{-1} . At lower J values the contribution of d to the total splitting remains nearly constant, but the term $(a - b/2 - c/2)$ begins to contribute, increasing approximately as $1/J$. From the equations for the coefficients

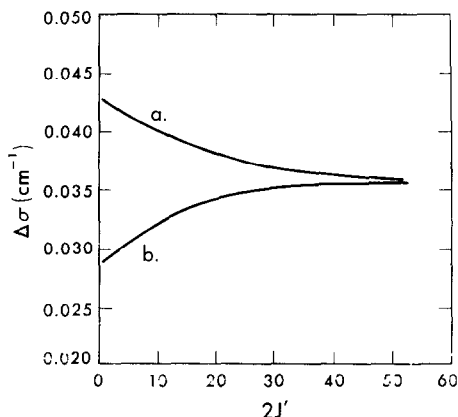


FIG. 4. Hyperfine splittings in the $A_1 {}^2\Pi_{1/2}$ state of HgD ($v' = 0$): a refers to the lower component of the lambda-doublet, and b to the upper.

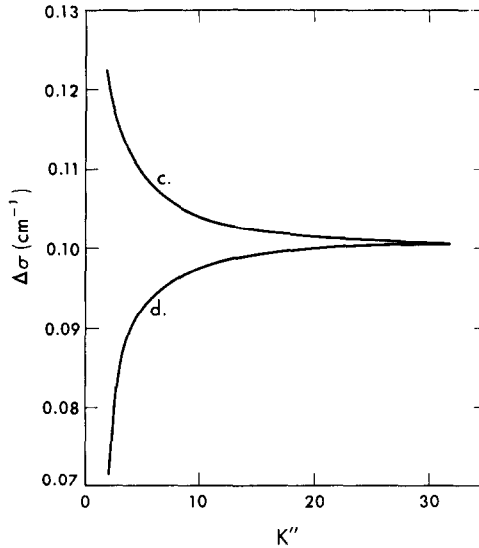


FIG. 5. Hyperfine splittings in the $X\ ^2\Sigma^+$ state of HgD ($v'' = 1$). c refers to the *upper* component of the spin-doublet, and d to the *lower*.

a , b , and c given by Townes and Schawlow, $(a - b/2 - c/2)$ should be negative for a $p\pi_{1/2}$ electron. Since d is positive and $+d$ applies to the upper level of the lambda-doublet, the splittings in the upper level should decrease as J becomes smaller, as is indeed observed. Similarly, $-d$ applies to the lower level, so the total splitting there should become larger than $d/2$, again in agreement with the observations.

From Fig. 5 may be obtained the value $b = 0.2010\text{ cm}^{-1}$ for the $v'' = 1$ level in the $^2\Sigma^+$ state. As K'' decreases, the splittings in the two components of the spin-doublet begin to differ. $(K'' + 1)/(2K'' + 1)$ becomes larger than $1/2$, while $K''/(2K'' + 1)$ becomes less than $1/2$, so the splitting in the lower component should decrease with decreasing rotation and that in the upper component should increase, as is observed, a behavior opposite to that of the components of the lambda-doublet in the $^2\Pi_{1/2}$ state. If the splittings are calculated from Eqs. (4) with coefficient c set equal to zero (it should be much smaller than b for this $p\sigma$ electron) the observed splittings agree less accurately with the equations as K'' decreases. The calculated values are too large for the upper component and too small for the lower component, the difference becoming greater as K'' decreases. These differences may be compensated somewhat by adding the effect of coefficient c ; it is possible to choose a value of c that will give good agreement with experiment for moderate to large values of K'' but not for very small K'' . This indicates that Eqs. (4) are not strictly applicable for small K'' . This is to be expected, for although case $b_{\beta J}$ coupling is the logical one for large K'' , case

$b_{\beta S}$ should be competitive for very small K'' , and for $K'' = 0$ in fact the coupling must be case $b_{\beta S}$.

Thus far only the variations of the hyperfine splittings with K'' have been discussed; they are the only ones given explicitly by the theoretical equations. Lacking a vibrational theory it still remains to explain at least qualitatively the observed variations with vibration (and also with isotopic mass). Consider first the ${}^2\Pi_{1/2}$ state where the splittings are $\pm d/2$ for large J and the coefficient d depends on $\langle 1/r^3 \rangle$. With increasing vibration or rotation the two nuclei move farther apart. When the hydrogen nucleus is farther from the mercury nucleus it is less effective in pulling electron probability density away from the mercury nucleus, so the electron is, on the average, closer to the mercury nucleus, an idea first suggested by Bohr in a communication to Mrozowski (15).³ Thus $\langle 1/r^3 \rangle$, and hence the splittings, should increase with increasing vibration or rotation, the change being greater the more anharmonic the molecule. Since HgH is much more anharmonic than HgD or HgT, the effect should be greatest there. Therefore the splittings in the energy levels of HgH were calculated also, using the experimental measurements of Porter.⁴ The only vibrational levels of ${}^2\Pi_{1/2}$ involved in his measurements are the $v' = 0$ and 1 levels. A small increase in d was indeed found from $v' = 0$ to 1, although the effect was difficult to determine exactly due to the large random scatter in the measurements. Unfortunately the Π state is much more harmonic than the ground state so the change in $\langle 1/r^3 \rangle$ is rather small even in HgH.

The same situation holds for the variation of d with rotation. Here also a very slight increase was found in HgH, but none was observable in HgD. The effect of this increase is seen partly in the steady drop of the Q_1 and Q_{12} curves in Fig. 3 of paper I, although changes in the ground state splittings also contribute to that drop.

In the ground state, which is much more anharmonic than the ${}^2\Pi$ state, the hyperfine interaction coefficients should change more noticeably with vibration and rotation. All three constants a , b , and c , depend on $\langle 1/r^3 \rangle$ and b depends on $\psi^2(0)$ as well (which changes in the same way as $\langle 1/r^3 \rangle$, increasing with internuclear separation). For large K the splittings are $\pm b/2$. The observations show a considerable decrease in b with increasing vibration. The decrease is most rapid in HgH, in accordance with its greater anharmonicity. This decrease is contrary to what might be expected, since

$$b = 2g_I \mu_0 \mu_N \left\langle \frac{8\pi}{3} \psi^2(0) - \frac{(3 \cos^2 \theta - 1)}{2r^3} \right\rangle \quad (5)$$

and the first term is the larger of the two. The fact that b decreases with vibration indicates that the second term increases more rapidly than the first. This pro-

³ Particularly the appended note on p. 537.

⁴ T. L. Porter, private communication, 1966.

duces interesting information about the molecular electronic wave function for the ${}^2\Sigma$ state. The wave function is such that with increasing internuclear separation either $\langle 1/r^3 \rangle$ increases faster than $\psi^2(0)$, or the angular distribution changes so that $(3 \cos^2 \theta - 1)$ increases faster than $\psi^2(0)$, or both. The electronic charge distribution is clearly not spherically symmetric, as that would give $(3 \cos^2 \theta - 1) = 0$.

Also observed is a decrease in b with increasing K , indicated by the drop in the Q curves in Fig. 3 of paper I. That drop is not due to the K'' factors in Eqs. (4) as was assumed there. This rotational effect is again greater in HgH than in HgD or HgT due to the greater anharmonicity of the former.

RECEIVED: November 17, 1969

REFERENCES

1. D. M. EAKIN AND S. P. DAVIS, *J. Opt. Soc. Amer.* **56**, 1422 (1966).
2. T. L. PORTER, *J. Opt. Soc. Amer.* **52**, 1201 (1962).
3. J. G. PHILLIPS AND S. P. DAVIS, "The Swan System of the C_2 Molecule and the Spectrum of the HgH Molecule," Univ. of California Press, Berkeley, 1968.
4. T. L. PORTER AND S. P. DAVIS, *J. Opt. Soc. Amer.* **52**, 1205 (1962).
5. T. L. PORTER AND S. P. DAVIS, *J. Opt. Soc. Amer.* **53**, 338 (1963).
6. W. F. MEGGERS AND R. W. STANLEY, *J. Res. Nat. Bur. Stand., Sect. A* **69**, 109 (1965).
7. D. M. EAKIN, PhD dissertation, University of California, Berkeley, 1966.
8. E. HULTHÉN, *Z. Phys.* **32**, 32 (1925); and **50**, 319 (1928).
9. (a) W. C. STWALLEY, PhD dissertation, Harvard University, Cambridge, 1968; (b) W. C. STWALLEY AND H. L. KRAMER, *J. Chem. Phys.* **49**, 5555 (1968); (c) W. C. STWALLEY, A. NIEHAUS, AND D. HERSHBACH, in "Vth International Conference on the Physics of Electronic and Atomic Collisions," Abstr. of papers, p. 639. Nauka Press, Leningrad, 1967.
10. T. L. PORTER, PhD dissertation, University of California, Berkeley, 1961.
11. Y. FUJIOKA AND Y. TANAKA, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo* **34**, 713 (1938).
12. J. H. VAN VLECK, *Phys. Rev.* **33**, 467 (1929).
13. G. HERZBERG, "Molecular Spectra and Molecular Structure." Vol. 1, 2nd ed. Van Nostrand, New York, 1950.
14. C. H. TOWNES AND A. L. SCHAWLOW, "Microwave Spectroscopy." McGraw-Hill, New York, 1955.
15. S. MROZOWSKI, *Z. Phys.* **95**, 524 (1935).