Band-Spectrum Analysis of Mercury Hydride*

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The emission spectrum of mercury hydride has been photographed in the second and third orders of a 21-ft concave grating in the region 2930–4550 Å. The light source was an electrodeless discharge tube containing a drop of mercury in an atmosphere of hydrogen and argon. Twenty-six bands of the A-X system and four bands of the B-X system have been analyzed, most of them to their predissociation limits. A table of these bands and a vibrational energy-level diagram are given. The behavior of the lambda-type doubling in the $^2\Pi$ state for which the electronic coupling is Hund's case a is compared with the theoretical prediction.

I N January 1960 the author undertook a detailed investigation of the optical emission spectrum of mercury hydride (HgH). The results of a study of the HgH band spectrum are presented here. Subsequent papers will treat the isotope shift and the magnetic hyperfine structure in the HgH spectrum.

The rotational analysis of the HgH band spectrum was facilitated by the use of techniques developed at Berkeley by the Analysis of Molecular Spectra program.[1] This project was initiated in 1959 by a grant of the National Science Foundation under the direction of Professor J. G. Phillips of the Department of Astronomy and the late Professor F. A. Jenkins for the detailed analyses of the spectra of selected diatomic molecules.

INTRODUCTION

Mercury hydride is a diatomic molecule which is produced in discharges through mixtures of hydrogen and mercury vapors. Its spectrum was first reported by Eder and Valenta in 1894,[2] but it was some time after that before the emitting molecule was identified. The first significant contributions to the rotational analysis of the HgH spectrum were made by Hulthén in 1925[3] and 1928.[4] In 1931, Rydberg[5] published rotational analyses of several additional bands together with the molecular constants for the excited electronic states. The paper of Fujioka and Tanaka in 1938[6] presented accurate analyses of four HgH bands with a common upper state and was thus used for a careful study of the molecular constants of the ground state. Techniques now available for high-resolution study of molecular spectra make it possible to reach the point where the complete rotational analysis of most of the HgH bands

expected to appear in the region 2930–4550 Å can be carried out.

The most prominent band system of HgH is $A\ ^2\Pi - X\ ^2\Sigma^+$.[7] The coupling in the ground state is necessarily Hund's case b, while the $^2\Pi$ state exhibits strong Hund's case a coupling in which the electronic spin $\mathbf{S}$ is strongly coupled to the internuclear axis. One consequence of this type of coupling in the $^2\Pi$ state is that all 12 allowed branches in such a transition should appear with comparable intensities, as, indeed, is the case for HgH. A second consequence is the existence of a large spin doubling in each rotational level corresponding to $\Omega = \Lambda \pm \Sigma$ with the result that each band appears as two sub-bands of six branches each, originating from the sub-states $A_1\ ^2\Pi_{\frac{1}{2}}$ and $A_2\ ^2\Pi_{\frac{3}{2}}$, respectively. For HgH,
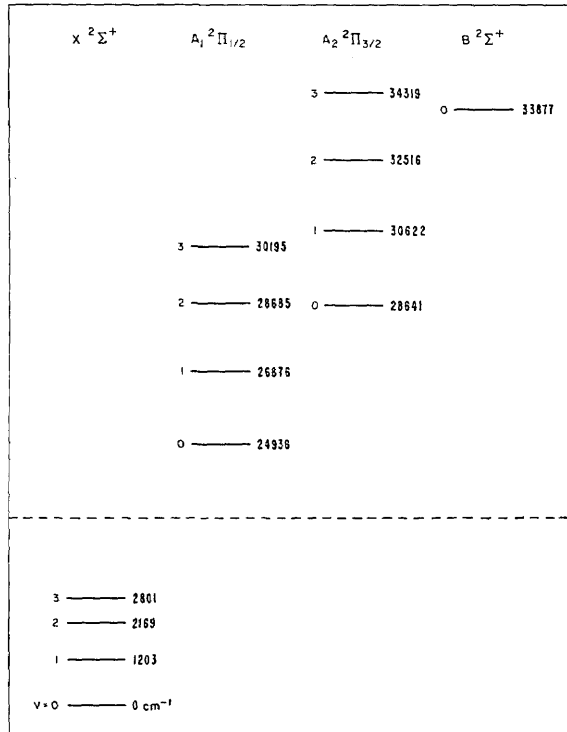

FIG. 1. Vibrational energy levels of mercury hydride.

[1] "Transactions of the Triple Commission for Spectroscopy," J. Opt. Soc. Am. **52**, 476 (1962).
[2] J. M. Eder and E. Valenta, Denkschr. Wien Akad. **61**, 401 (1894).
[3] E. Hulthén, Z. Physik **32**, 32 (1925).
[4] E. Hulthén, Z. Physik **50**, 319 (1928).
[5] R. Rydberg, Z. Physik **73**, 74 (1931).
[6] Y. Fujioka and Y. Tanaka, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **34**, 713 (1938).
[7] G. Herzberg, *Molecular Spectra and Molecular Structure, Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed., Vol. I.

the spin doubling is about 3700 cm^{-1} and is thus the strongest known example of Hund's case a. For most of the bands in this system $B'-B''$ is positive, giving bands degraded to the violet.

The second excited electronic state of HgH is another $^2\Sigma^+$ state, and the transition $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$ is observed. In such a transition six branches are allowed, but two of them are expected to decrease so rapidly in intensity that their observation is limited to lines near the origin. Two other excited electronic states are known for HgH. Both are of the $^2\Sigma^+$ type and give rise to transitions to the ground state. These last two band systems will not be treated in this paper.

The band spectrum of HgH begins at about 4550 Å and extends to lower wavelengths. Because of the experimental considerations necessary to produce the high accuracy desired in this work, a lower limit of 2930 Å was placed on the accessible spectral region. For the nine upper vibrational levels: $v'=0$–3 of $A_2\ ^2\Pi_{\frac{3}{2}}$, $v'=0$–3 of $A_1\ ^2\Pi_{\frac{1}{2}}$, and $v'=0$ of $B\ ^2\Sigma^+$, and for the four lower levels: $v''=0$–3 of $X\ ^2\Sigma^+$, all but one of the thirty-six vibrational transitions between these levels lie in this region, and practically no other observed bands lie in the same region. An energy-level diagram showing these levels is given in Fig. 1.

EXPERIMENTAL

The HgH light source was of the electrodeless discharge type. This choice was based on the need of a light source which would operate efficiently with small amounts of mercury, since it had to be suitable for experiments on the hyperfine structure of HgH for which expensive mercury isotopes were available only in small quantities. Such lamps are conveniently excited with a microwave generator and require normally only small amounts of material.

The HgH lamp was made of fused silica, and consisted of a 12-cm section of 7-mm-o.d. tubing attached to a 5-cm length of 22-mm-o.d. tubing which served as a hydrogen reservoir. It contained about 1 g of natural mercury in an atmosphere of 1.0 mm Hg of hydrogen and 0.25 mm Hg of argon as a carrier gas. Operation of the lamp tended to drive the hydrogen onto the inner walls of the tube. Although it was found that occasional heating could drive the hydrogen from the walls, it was much more convenient to provide the hydrogen reservoir at one end of the tube. None of the dimensions are critical, and, as long as there are a hydrogen reservoir and mercury in excess of about 300 mg, such a lamp can operate for many hours as an intense, constant HgH source.

The lamp was excited with a Raytheon model CMD microtherm exciter using the vertical antenna with a wedge reflector. The tube was placed vertically against the antenna at such a height that, at full microwave power output, the discharge extended about 1.5 cm above the mercury pool. The air stream from a small fan was directed at the bottom portion of the tube and served to keep the vapor pressure of mercury low enough that the mercury spectrum did not quench the HgH spectrum. With this arrangement the volume just above the mercury pool emitted a rich HgH spectrum sustained by mercury distilling upward into it from the pool. The mercury then condensed on the wall of the tube above the discharge and eventually dropped back to the bottom. In this manner the mercury recycled allowing continuous operation of the lamp.

The HgH spectrum was photographed with a 21-ft concave grating in a Paschen mounting with a plate factor in the first order of about 1.3 Å/mm. The region 2930–3300 Å was recorded in the third order, and the region 3300–4550 Å in the second order. The resolution was estimated at somewhat less than 100 000 in the first order. A resolution of approximately 300 000 is required to resolve the hyperfine structure in HgH. In the second order the band lines were quite sharp, although not as sharp as the comparison lines. In the third order, a slight broadening was evident although no structure could be resolved. The exposure times were typically of the order of 2 min for the stronger bands to 30 min for the weaker bands.

The arrangement of the appropriate spectra on the photographic plate was similar to that originally adopted by the Analysis of Molecular Spectra project.[1] The HgH spectrum was recorded between two separate exposures of the thorium spectrum from a thorium iodide electrodeless discharge lamp. The interferometrically measured lines in the thorium spectrum[8] served as the comparison spectrum. On the other side of one of the thorium spectra there was recorded a strip of Edser–Butler heterochromatic fringes.[9] Such fringes are produced by passing through the spectrograph slit the central portion of the ring system of a Fabry–Perot interferometer with a high-pressure xenon-arc light source. Successive fringes are separated by a wave number difference which is determined by the plate separation of the interferometer and which may be considered constant over the spectral range covered by an 18-in. photographic plate. These fringes were used to determine the shape of the dispersion curves between the interferometrically measured thorium comparison lines on the adjacent strip.

The two sets of comparison spectra were photographed immediately before and after the molecular spectrum and served as a check on any shift of the molecular spectrum during the exposure because of changing atmospheric conditions. It was in no case necessary to correct for such a shift. In the third-order molecular spectrum, second-order comparison lines were used. In such cases there are normally small corrections which have to be applied to the measured wavelengths. However, because of the slight broadening of

[8] W. F. Meggers and R. W. Stanley, J. Research Natl. Bur. Standards **61**, 95 (1958).

[9] F. S. Tompkins and M. Fred, J. phys. radium **19**, 409 (1958).

the third-order molecular lines, no such shift could be detected.

Finally, each plate contained a set of density marks produced by passing a continuum through a step-weakener placed immediately in front of the plate. By means of the known transmissions of the several steps, the density-intensity relationship for the plate could be obtained.

The plates were measured on a photoelectric comparator similar to the type described by Tompkins and Fred.[10] By means of a Giannini–Datex encoder attached to the output, the screw reading, the density, and an identifying symbol could be punched directly onto an IBM card for each line. The deck of cards representing the measurements for a single plate or for several sections of a plate were processed with an IBM 704 computer. The computer output consisted of the molecular wavelengths, vacuum wavenumbers, and

TABLE I. Emission bands of mercury hydride.

Band	λ head	σ head	Intensity
A_1 $^2\Pi_{\frac{1}{2}} - X$ $^2\Sigma^+$			
0–3	4519.493	22120.17	4
0–2	4395.712	22743.05	15
0–1	4218.763	23696.96	50
1–3	4155.275	24059.01	2
1–2	4050.724	24679.98	10
0–0	4017.328	24885.13	100
1–1	3900.346	25631.49	2
2–3	(3864.554)	(25868.87)	0
2–2	3774.422*	26486.60*	2
1–0	3728.461	26813.09	40
3–3	(3652.507)	(27370.64)	0
2–1	3644.375	27431.71	8
3–2	3575.170	27962.71	3
2–0	3495.811	28597.48	10
3–1	3431.112 (R)	29136.71	5
3–0	3301.157 (R)	30283.69	2
A_2 $^2\Pi_{\frac{3}{2}} - X$ $^2\Sigma^+$			
0–3	3874.465	25802.70	3
0–2	3783.610	26422.28	10
0–1	3651.998	27374.47	30
1–3	3698.200*	27783.75*	2
1–2	3519.837	28402.29	4
0–0	3500.324	28560.62	80
1–1	3405.887	29352.50	2
2–3	(3368.624)	(29677.19)	0
2–2	3299.940	30294.85	2
1–0	3274.134	30533.63	25
2–1	3199.943	31241.53	12
3–3	(3175.632)	(31480.69)	0
3–2	(3114.709)	(32096.42)	0
2–0	3084.179	32414.12	5
3–1	3025.900	33038.40	2
3–0	(2923.334)	(34197.51)	···
B $^2\Sigma^+ - X$ $^2\Sigma^+$			
0–0	2949.554 (R)	33893.52	15
0–1	3057.652 (R)	32695.36	25
0–2	3148.489 (R)	31752.08	3
0–3	3218.740	31059.09	2

intensities which were then ready for analysis into the several bands.

BAND SPECTRUM

The 36 possible bands connecting the 13 vibrational levels studied are listed in Table I. The measured wavelength and vacuum wavenumber of the head, and the estimated intensity on a scale of 100 are listed for each band. The six bands designated by parentheses are those which were not found, either because of weak intensity or, in one case, because the band lay outside the spectral region photographed. Bands designated by (R) are degraded to the red. An asterisk indicates that the line at the head of the designated band had to be calculated using combination relationships, although most of the remaining lines of the band were identified.

The spectrum of HgH is a well-known example of rotational predissociation.[11] As a consequence, the bands are observed to terminate at very low values of N for the ground state: $N=31$, 24, 16, and 8 for $v''=0$, 1, 2, and 3, respectively. The breakoff of a band is normally characterized by a sharp line, followed by a broad line that is barely measurable, and then followed by a very broad smear. As an illustration of this phenomenon, the termination of several branches in the 0–2 band of the A_1-X system is shown in Fig. 2.

Because of the termination of each branch at a known value of J, it is possible to know exactly how complete an analysis has been achieved for each band. In this work most of the bands have been analyzed to their predissociation limits. The rotational analyses of the individual bands are not included in this paper. They will be published at a later date as part of a complete analysis of all the band systems of the HgH spectrum. For the bands in the high-wavelength region, and for the prominent bands down to 3300 Å, the accuracy of the wave numbers of the molecular lines is about ±0.02 cm⁻¹. For the weaker bands below 3800 Å and the third-order bands, the uncertainty may be up to twice this value.

The HgH spectrum contains several perturbations, some of which are well-known. For example, strong perturbations exist between the levels of $^2\Pi_{\frac{1}{2}}$, $v'=2$ and $^2\Pi_{\frac{3}{2}}$, $v'=0$ at $J'=9\frac{1}{2}$ and $10\frac{1}{2}$ due to nearly equal energies. These perturbations have been studied in detail by Rydberg.[5] Additional strong perturbations were found in the levels of $^2\Pi_{\frac{3}{2}}$, $v'=1$ at $J'=10\frac{1}{2}$ (also reported by Rydberg), $21\frac{1}{2}$ and $22\frac{1}{2}$. However, no perturbation of similar magnitude was found at $^2\Pi_{\frac{3}{2}}$, $v'=2$, $J'=10\frac{1}{2}$ as implied by Rydberg.

For $^2\Sigma^+$ states the spin doubling is expected to be given by $\gamma(N+\frac{1}{2})$ where γ is a constant. In the B $^2\Sigma^+$, $v=0$ levels of HgH the observed splitting reaches a maximum of 7.22 cm⁻¹ at $N=9$, then decreases slowly to nearly zero at $N=19$, which observations are similar to those of Rydberg.[5] In this work it was possible to

[10] F. S. Tompkins and M. Fred, J. Opt. Soc. Am. 41, 641 (1951).
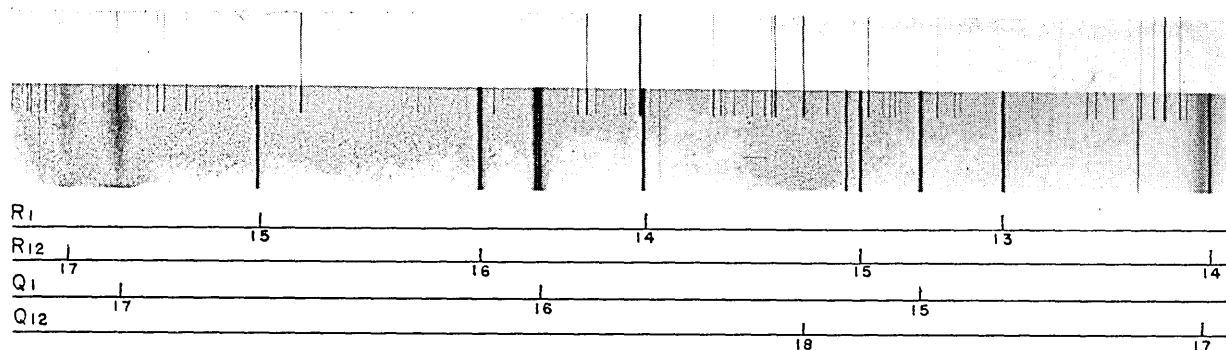
[11] See reference 7, pp. 413, 427.

FIG. 2. Rotational predissociation in the $^2\Pi_{\frac{1}{2}}-{}^2\Sigma^+$ 0–2 band of mercury hydride.

extend the analysis of this vibrational level to $N = 24$ at which point the splitting has increased rapidly to nearly 50 cm^{-1}. The analysis of the $B-X$ system also shows that the "forbidden" Q branches appear very strongly in the 0–1 and 0–2 bands, but are not observed in the 0–0 and 0–3 bands. These results are also in agreement with those of Rydberg. The explanation for these observations on the spin doubling and the Q-branch intensities in this state is uncertain.

Lambda-Type Doubling in the $^2\Pi$ State

In electronic states with $\Lambda \neq 0$ each rotational level may split into two components, a phenomenon known as lambda-type doubling. This effect is an uncoupling phenomenon and arises from the fact that there is a slight interaction between the rotation of the nuclei and the orbital angular momentum $\mathbf{L}$, especially at high values of J.[12] The theoretical treatment of this problem has been given in detail by Mulliken and Christy[13] who also compared their predictions with the experimental evidence available at that time for the $v = 0$, 1 vibrational levels of $^2\Pi_{\frac{1}{2}}$. Now that information is available for several more HgH vibrational levels, it is of interest to compare the observed behavior of the splittings to the expected behavior.

For a $^2\Pi_{\frac{1}{2}}$ state the splitting is expected to be given by

$$\Delta\sigma_{cd}(j) = a(J + \tfrac{1}{2}),$$

where a is a constant. In the HgH spectrum, the splitting is not observed to increase linearly with J but somewhat more slowly. For example, for $v = 0$ the increment

$$\Delta\sigma_{cd}(j+1) - \Delta\sigma_{cd}(j)$$

has the value 3.36 cm^{-1} at $J = \frac{1}{2}$, but has decreased to 2.05 cm^{-1} at $J = 18\frac{1}{2}$. An exception to this behavior is the level $v = 3$ for which the value of $\Delta\sigma_{cd}(j)/(J + \frac{1}{2})$ increases with J. The value of a was calculated by examining the behavior of $\Delta\sigma_{cd}(j)/(J + \frac{1}{2})$ as J approached zero. The results of this calculation are shown in Table II.

The behavior of the lambda-type doubling in the $A_2\,^2\Pi_{\frac{3}{2}}$ state is more complex. In this state the splitting is given by

$$\Delta\sigma_{dc} \sim J^3,$$

but the magnitude of the splitting is expected to be smaller than that in the $^2\Pi_{\frac{1}{2}}$ state by a factor of $Y^2 = (A/B_v)^2$, where A is the spin doubling in the $^2\Pi$ state. For HgH, Y has the value of about 600. It turns out, however, that the splitting does not increase with J^3. In the levels $v = 0$, 1 the splitting becomes measurable at about $J = 8\frac{1}{2}$, and increases slowly to about 0.5 cm^{-1} around $J = 25\frac{1}{2}$. For $v = 2$, 3, the splitting is measurable at all J values and increases somewhat more rapidly.

CONCLUSION

This work has enabled most of the lines in the spectrum of mercury hydride in the region 2930–4550 Å to be identified and assigned to thirty bands belonging to the electronic transitions $B\,^2\Sigma^+$, $A_1\,^2\Pi_{\frac{1}{2}}$, $A_2\,^2\Pi_{\frac{3}{2}}$-$X\,^2\Sigma^+$. Although the Hund's case a coupling in the $^2\Pi$ state is the strongest such case known, investigation of the behavior of the lambda-type doubling shows that there are departures at high J values from the behavior theoretically predicted on the basis of such a coupling scheme.

The study of the HgH spectrum is continuing at Berkeley as part of the Analysis of Molecular Spectra Program. Part of the effort will be directed at extending the analysis to 2500 Å to include two additional band systems. Upon completion of this work, a complete report, including the rotational analyses of all the bands, will be published.

TABLE II. Lambda-type doubling for the $A_1\,^2\Pi_{\frac{1}{2}}$ state of mercury hydride: The limiting value of $a = \Delta\sigma_{cd}(j)/(J + \frac{1}{2})$ at $J = 0$.

v	a
0	3.360±0.003 cm^{-1}
1	2.84 ±0.01
2	2.04 ±0.02
3	0.67 ±0.01

[12] See reference 7, p. 226.
[13] R. S. Mulliken and A. Christy, Phys. Rev. 38, 87 (1931).