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Emission Bands in the $3p^1\Pi_{cd}-1s^1\Sigma$ System of the Hydrogen Molecule

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The $3p^1\Pi_{cd}-1s^1\Sigma$ band system of the hydrogen molecule, heretofore observed only in absorption, has been discovered in emission. Ten bands from the first three vibrational levels of the excited state are analyzed and the rotational and vibrational constants are derived. The d component levels of the Λ type doubling are found to be strongly perturbed whereas the c components appear to be quite regular. The most significant of the constants derived are as follows: $T_e=113908$ cm^{-1}, $B_e=30.56$ cm^{-1} and $\omega_e=2353$ cm^{-1}.

Introduction

This paper is concerned with the identification and analysis of a number of emission bands in the $3p^1\Pi_{cd}-1s^1\Sigma$ system of H_2 and with the molecular constants derived therefrom. This band system was discovered by Hopfield[1] who found a v' progression in absorption lying in the extreme ultraviolet between 830 and 770A. Before the present study this system had not been observed in emission. Beutler, Deubner and Junger[2] and Beutler and Junger,[3] by means of the isotope effect showed that the absorption progression began with the $v=3$ level of the upper state. The $v=0$, 1 and 2 vibrational levels are missing. This had previously been suggested by Richardson[4] as a possible explanation of the bands, since the heat of dissociation and Rydberg denominator indicated by this progression were not compatible with other known data on H_2, if the first member of the progression were the $0-0$ band.

Beutler, Deubner and Junger's thorough study of this absorption spectrum fixed the identification of the excited electronic level as the $3p^1\Pi_{cd}$ state and this conclusion is further substantiated by the results of the present study. These authors found also that the absorption bands were broadened and diffuse because of predissociation beginning at the $v=3$ level and autoionization beginning at the $v=6$ level. The presence of these phenomena explains the previous failure to find this band system in emission. The vibrational levels $v=0$, 1 and 2 should, however, give rise to emission bands and a number of these have now been found and are described in the following paragraphs. It is not possible however, as just noted, to obtain emission bands from higher vibrational levels than the third, hence our data are not so complete as might be desirable.

Experimental Methods

The procedure used for excitation of the hydrogen spectrum has been described in an earlier paper[5] and the experimental results of this former study have been used in the present investigation. Additional data have been secured, however, in the region of the short wave-length end of the spectrum. This has been made possible through the use of a new spectrograph built in the shop of the University of California physics department. This spectrograph contains a grating ruled at the Johns Hopkins University, with 11,800 lines per cm and with a radius of 42 cm. The grating mounted at normal incidence is very fast and gives spectra relatively free from background. Most of the data of the present work were obtained with the 2 meter spectrograph described earlier[5] and hence the dispersion obtained on the plates is about 3.5A per mm. The small spectrograph mentioned above gives a dispersion of about 20A per mm and so for the very faint lines photographed only with this instrument, the probable error is perhaps as much as 0.05A. In this later study hydrogen lines from the former work have been used as standards.

Rotational Analysis

The intervals between vibrational levels (ΔG_v values) in the $3p^1\Pi_{cd}$ state may be determined

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[1] J. J. Hopfield, Nature **125**, 927 (1930).

[2] Beutler, Deubner and Junger, Zeits. f. Physik **98**, 181 (1935).

[3] Beutler and Junger, Zeits. f. Physik **100**, 80 (1936).

[4] O. W. Richardson, *Molecular Hydrogen and its Spectrum* (Yale University Press, 1934), p. 303.

[5] C. R. Jeppesen, Phys. Rev. **44**, 165 (1933).

directly for $v>3$ from the absorption progression previously mentioned. For $v<3$ approximate ΔG_v values may be obtained from the same data by extrapolation. Since a rather complete analysis of the lower $1s^1\Sigma$ state is known[5] we can then find the approximate position of each expected emission band in our system. The rotational analysis may then be carried out by the usual methods. The chief difficulty with such analysis lies in the extensive overlapping of bands, so that chance coincidences are very frequent. This is especially troublesome when, as in the present instance, the bands under consideration are comparatively low in intensity and are overlapped by other systems of greater strength. For this reason the tentative assignments given to a number of lines are quite doubtful and are not included in the data given here. The bands for which the assignments appear to be fairly certain are given in Table I. Since all of the numerical results deduced from the ten bands given in the table are consistent and are compatible with previously known results, it would appear that the essential correctness of the identifications cannot be doubted. Table I gives

TABLE I. *Emission bands of the* $3p^1\Pi_{cd}-1s^1\Sigma$ *system.*

K	*I*	*R* BRANCH	*I*	*P* BRANCH	*I*	*Q* BRANCH
0−1 band $\nu_0=108715$						
0	1	108773.1				
1	3	784.9			2	108655.4
2	0	744.8	1	108437.4	1	549.6
3	2	655.4*	3	227.2	2	391.8
4	1	523.8?	1	107972.5	0	182.8
5			6	666.2*	1*b*	107929.1
0−2 band $\nu_0=104791$						
0	3	104849.3				
1	4	865.8			4	104738.0
2	—	—	2*d*	104528.5	2	642.5
3	3	764.6	3	336.9	3	501.9
4	2	657.6	1	104.1	2	317.8
5			1	103831.4	1	093.2
0−3 band $\nu_0=101092$						
0	1	101151.3				
1	4	174.5			6	101045.5
2	0	159.0	2	100850.2	3	100963.0
3	1*b*	102.3	4	673.0*	3	838.2
4			1*d*	463.8	4	673.0*
5			1	215.5	3	475.3
1−1 band $\nu_0=110939$						
0						
1	2	110989.8			3	110875.1
2	1	934.7	1*bd*	110646.6*	2	763.1
3	1	820.4	4	433.5	3	596.2
4	1*bd*	646.6*	2	162.4	1	376.3
5	1	387.6?	2	109840.2	1*d*	104.6
1−3 band $\nu_0=103322$						
0	1*d*	103374.5				
1	3	386.4			4	103272.4*
2	1	355.9	2	103072.1	3*d*	180.5
3	4	272.4*	3	102886.4	3	048.5
4			1	659.7	—	—
5			2*b*	392.4	0	102675.6
1−4 band $\nu_0=99848$						
0	3*b*	99899.7*				
1	5	918.8			6	99803.6
2	3*b*	899.7*	2*d*	99617.4	3	725.5*
3	2	834.4	3	447.3	4	609.6
4	3	725.5*	2	243.4	3*b*	462.3
5			4	004.9	2	265.6
1−5 band $\nu_0=96605$						
0	2	96659.5				
1	4	684.2			5	96567.9
2	5	668.9	1	96390.3	4	500.3
3	3	626.5	3	237.4	2	401.0
4			1	054.7	—	—
5			2	843.0	1	108.1
2−2 band $\nu_0=109113$						
0	2	109161.6				
1	2	166.7			3	109051.8
2	0	119.6	3	108844.1	1	108945.2
3	0*b*	012.3	2	638.7	3	784.9
4	2*d*	108858.0	0	384.6		
5			3	084.5		
2−3 band $\nu_0=105421$						
0	1	105471.7				
1	3	480.4			4	105365.2
2	1	442.5	2	105168.8	2	269.3
3	1	356.6	2	104980.6	1	127.3
4			3	750.0	1	104940.9
5			1	474.4	0	711.1
2−5 band $\nu_0=98703$						
0	—	—				
1	4	98778.1*			5	98660.8
2	1	756.3	1	98488.6*	5	591.6
3	2	709.8	4	335.5*	3	481.5
4	1	621.0	1	148.2	4	335.5
5			1	97930.5	00	159.3

the origin of each band and the wave number of each line in the band together with an eye estimate of its intensity. Lines indicated by an asterisk are known blends. The letter "*d*" or "*b*" following the intensity estimate of a line indicates that it is either diffuse or broad as the case may be.

DERIVATION OF CONSTANTS

As has been found previously[5] the rotational energy function for a state having the characteristics of the present $3p^1\Pi_{cd}$ level may be written:

$$F=B_i^x[K(K+1)-\Lambda^2] +D_i^xK^2(k+1)^2+F_i^xK^3(K+1)^3. \quad (1)$$

The subscript i indicates the double valued nature of the function, one set of rotational constants being necessary for the c component levels and another for the d components of the Λ type doubling. The superscript x indicates that these are the so-called "effective" values of the constants. In analogy to the $2p^1\Pi_{cd}$ level discussed earlier[5] it should be emphasized that in our case the "true" rotational constants are equal to the effective values given by the c component levels (our B_c^x, D_c^x etc.).

The values of B_c^x as a function of v determined directly from the wave numbers are given in the first column of Table II. In the second column of this table are given the smoothed values from the following linear equation:

$$(B_c^x)_v=30.56-1.643(v+\tfrac{1}{2}). \quad (2)$$

The third column of Table II records the observed $(B_d^x)_v$ values. In the case of the d component levels we find that the Δ_2F values, from which the rotational constants are determined, are quite irregular. It is therefore not possible to determine accurate values of $(B_d^x)_v$ and the values given in the table are to be considered only as approximations. They were determined by the graphical method described by Birge.[6] The last column in Table II gives the values of $(B_d^x)_v$ determined graphically from a straight line drawn through the data of column three. This last column is included only to indicate the futility of any attempt to represent these data by a simple function that will give a reasonable extrapolated value of $(B_d^x)_e$. The values of $(B_i^x)_v$ are shown graphically in Fig. 1.

TABLE II. *Values of* $(B_i^x)_v$ *in* cm^{-1} *units.*

v	OBS. $(B_c^x)_v$	CALC. $(B_c^x)_v$	OBS. $(B_d^x)_v$	CALC. $(B_d^x)_v$
0	29.73	29.74	31.22	30.92
1	28.11	28.10	28.65	29.17
2	26.43	26.45	27.62	27.43

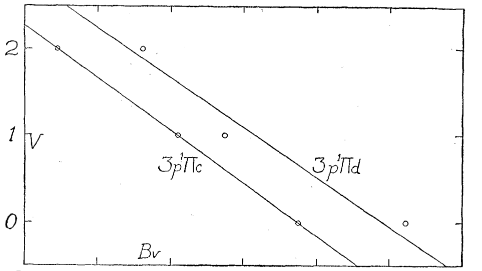

FIG. 1. Graphical representation of B_c^x and B_d^x as functions of v.

While the given values of $(B_d^x)_v$ have relatively large probable errors (by comparison with the $(B_c^x)_v$ values which are accurately determined by analytic methods) they deviate from a straight line by amounts many times greater than their individual probable errors. It is apparent from Fig. 1 that if the B_d^x values should be represented by the same type of function that fits the B_c^x data so well, the rotational levels of the $v=1$ state are crowded together more closely than they should be and the levels of the $v=0$ and $v=2$ states are spread more widely apart. Thus

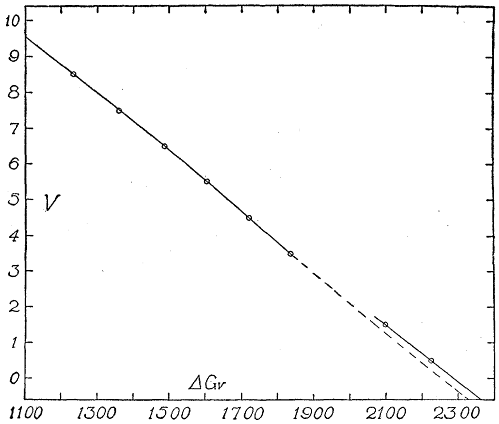

FIG. 2. Graphical representation of $\Delta G : v$. Data for $v>3$ are from the absorption spectrum (Beutler, Deubner and Junger) and for $v<2$ are from the present study of the emission spectrum.

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[6] R. T. Birge, National Research Council Bulletin, No. 57, *Molecular Spectra in Gases* (1937), p. 172.

the evidence that the d component levels of the $3p^1\Pi_{cd}$ state are perturbed is quite conclusive. The c component levels, on the other hand, appear to be entirely regular. This is the same situation as that which exists in the case of the $2p^1\Pi_{cd}$ state and which has been discussed in a previous paper.[5]

The vibrational term differences have already been obtained[1, 2] from the data of the absorption spectrum. These data however do not give as accurate a value of ΔG_e as can be obtained from the present work. In the first place the $v=0$, 1 and 2 levels are missing in the absorption spectrum and in the second place the origins of the bands cannot be closely determined until the rotational structure is analyzed. In Fig. 2 is indicated graphically the ΔG_v values obtained from the emission spectrum (low values of v) and from the absorption spectrum (high values of v). The directly determined ΔG_v values from the present study are $\Delta G_{\frac{1}{2}}=2226$ and $\Delta G_{1\frac{1}{2}}=2099$ cm^{-1} respectively. The extrapolated value of ΔG_e is then 2353 ± 10 cm^{-1} as compared with 2316 ± 20 cm^{-1}, derived[2] from the absorption spectrum.

TABLE III. *Constants of the* $3p^1\Pi_{cd}$ *state.*

T_e	113908 ± 10 cm^{-1}	r_e	1.044A
B_e	30.56 ± 0.04 cm^{-1}	α_e	1.643 cm^{-1}
ΔG_e	2353 ± 10 cm^{-1}	$2x_e\omega_e$	227 cm^{-1}
I_e	0.9051×10^{-40} g cm^2		

A summary of the values of the important constants is given in Table III.

It may be remarked that in the calculation of T_e as given in Table III the presence of Λ in the rotational energy function (Eq. (1)) was taken into consideration.

A search for the $3p^1\Pi_{cd}-1s^1\Sigma$ band system in the emission spectrum of D_2 has been made, but because of the very small intensity of the D_2 spectra on the photographs thus far obtained and measured, the result of this study is inconclusive.

JULY 1, 1938 PHYSICAL REVIEW VOLUME 54

The Classification of the Spectrum of Singly Ionized Tin. Sn II

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The spectrum of Sn II, as excited in a hollow cathode discharge in helium, has been photographed from 800A to 10,000A. Some 70 new lines have been classified and 28 new levels established. A few changes have been made in the levels and classifications previously made by Green and Loring, Narayan, and Lang. The $5s^2ms$, $-mp$, $-md$ and $-mf$ series have been extended, and the ^2F levels have been resolved for the first time. Six members of the $5s^2mg\ ^2G$ series have been located and used to make a new determination of the ionization potential of Sn II as $118{,}017\pm3$ cm^{-1}. The classification has been checked by series relations, Zeeman patterns, and by comparison with the isoelectronic spectra In I and Sb III. Irregularities in the ^2S and ^2D terms are explained qualitatively by consideration of interactions with perturbing terms from the configuration sp^2.

THE first classifications of Sn II were made independently by Green and Loring[1] and by Narayan and Rao[2] and were in substantial agreement. Green and Loring, using vacuum arc data, supplemented by data of R. J. Lang in the extreme ultraviolet, and with the help of a few Zeeman effects, classified thirty of the stronger lines, fixing nineteen low levels. Two levels each were found in the low normal ^2S, ^2P, ^2D and ^2F series, and the ^2D and ^2S levels from the configuration sp^2 were located. Lang[3] later rephotographed the spectrum with a hollow cathode discharge, and made a few corrections and additions, notably the ^4P terms from sp^2. No high terms were found in these researches and the ionization potential was determined only roughly by Green and Loring, who fixed it

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[1] Green and Loring, Phys. Rev. **30**, 574 (1927).

[2] Narayan and Rao, Zeits. f. Physik **45**, 350 (1927).

[3] Lang, Phys. Rev. **35**, 445 (1930).