

Bands in the Extreme Ultraviolet Emission Spectrum of the H^1H^2 Molecule

C. RULON JEPPESEN, *University of California*

(Received February 15, 1934)

By using a two meter grazing incidence vacuum spectrograph, the extreme ultraviolet emission spectrum of a mixture of about 60 percent ordinary hydrogen and 40 percent "heavy" hydrogen has been photographed. All together twelve bands have been identified as belonging to the $2p\ ^1\Pi_{ca}-1s\ ^1\Sigma$ system of the H^1H^2 molecule. Analysis of these bands indicates that the rotational and vibrational constants for the H^1H^2 molecule are the same to within ex-

perimental error as those derived from the theory of the isotope effect. *There is, however, an extremely large electronic isotope shift of 135 cm^{-1} units.* The apparent vibrational perturbation found previously in the $v=3$ level of the $2p\ ^1\Pi_{ca}$ state of the H^1H^1 molecule has its counterpart in the same level of the H^1H^2 molecule where its magnitude is about 4.3 cm^{-1} units, compared to 10.4 cm^{-1} for H^1H^1 .

INTRODUCTION

FOLLOWING the discovery of a hydrogen isotope of mass 2, many investigators have studied the various properties of this new atom and the molecules formed by its combinations with other atoms. The present paper deals with the results so far obtained in an investigation of the extreme ultraviolet spectrum of a mixture of about 60 percent ordinary hydrogen and 40 percent of the "heavy" isotopic hydrogen.

EXPERIMENTAL PROCEDURE

The spectrograph and the type of discharge tube used in the present study have been described previously.¹ A quantity of the heavy isotopic hydrogen was generously supplied by Professor G. N. Lewis of the chemistry department. Exposures of one hour duration using power from a one kw 25,000 volt transformer were sufficient to obtain more than 2500 lines in

the spectrum between 800 and 1375A. Known lines in the spectrum of H^1H^1 , the wave-lengths of which had been previously determined,¹ were used as standards for the reduction of the plates.

ANALYSIS

The well-known theory² of the isotope effect in band spectra allows the calculation of the rotational and vibrational constants for the molecule H^1H^2 from the known values of these constants for H^1H^1 . The mass of H^2 has been found by Bainbridge³ to be 2.01363. This leads to a value of the constant ρ equal to 0.86616. The equations given in the previously-mentioned¹ study of the H^1H^1 bands, together with this value of ρ , then lead to the following equations for the respective constants of the H^1H^2 molecule.

For the $1s\ ^1\Sigma$ (normal) state of the molecule B_v from $v=0$ to $v=5$ is given in cm^{-1} units by the equation:

$$B_v^i = 45.668 - 1.99305(v + \frac{1}{2}) + 0.0384948(v + \frac{1}{2})^2 - 0.00316885(v + \frac{1}{2})^3. \quad (1)$$

Because of the extreme curvature of the $B_v : v$ function, another equation is necessary for the fitting of B_v for higher values of v . Accordingly for $v=6$ to $v=9$ the following equation may be used.

$$B_v^i = 45.350 - 1.81546(v + \frac{1}{2}) + 0.00590989(v + \frac{1}{2})^2 - 0.00117286(v + \frac{1}{2})^3. \quad (2)$$

For all observed values of v , D_v^i is given by the equation:

$$D_v^i = -0.0261849 + 0.00065863(v + \frac{1}{2}). \quad (3)$$

¹ C. R. Jeppesen, Phys. Rev. **44**, 165 (1933).

² W. Jevons, *Report on Band Spectra of Diatomic Molecules*, Cambridge (1932).

³ K. T. Bainbridge, Phys. Rev. **44**, 57 (1933).

F_v^i , which may be assumed equal to F_e^i , is found to be $F_v^i = 2.1876 \times 10^{-5} \text{ cm}^{-1}$. (4)

And finally, ΔG_v is given with sufficient accuracy from $v = -\frac{1}{2}$ to $v = 6\frac{1}{2}$ by the equation:

$$\Delta G_v^i = 3826.0 - 197.03(v + \frac{1}{2}) + 6.0733(v + \frac{1}{2})^2 - 0.42776(v + \frac{1}{2})^3. \quad (5)$$

For the $2p \ ^1\Pi_{cd}$ (C) state of the H¹H² molecule the corresponding equations, which are valid for all observed values of v , are as follows:

$$(B_c^x)_v^i = 23.473 - 0.85564(v + \frac{1}{2}) - 0.0673705(v + \frac{1}{2})^2 + 0.00800339(v + \frac{1}{2})^3, \quad (6)$$

$$(D_c^x)_v^i = -0.0117966 + 0.000403285(v + \frac{1}{2}), \quad (7)$$

$$(F_c^x)_v^i = 7.9813 \times 10^{-6}, \quad (8)$$

$$(B_d^x)_v^i = 23.8086 - 1.02035(v + \frac{1}{2}), \quad (9)$$

$$(D_d^x)_v^i = -0.0120466 + 0.00039199(v + \frac{1}{2}), \quad (10)$$

$$(F_d^x)_v^i = 8.31957 \times 10^{-6}. \quad (11)$$

The subscripts c or d as the case may be, indicate that the constant in question should be ascribed to the c or d component levels. The superscript x indicates that the values of B , D and F given are "effective" values of these constants to take account of the Λ -type doubling. The values of ΔG_v for the $2p \ ^1\Pi_{cd}$ state are given by the equation:

$$\Delta G_v^i = 2140.3 - 133.44(v + \frac{1}{2}) + 11.940(v + \frac{1}{2})^2 - 1.22607(v + \frac{1}{2})^3. \quad (12)$$

These equations not only allow the calculation of the rotational energy functions for each electronic state, from which the ΔF values may be obtained, but they may also be used to find the position of any band in the system.

A search for lines satisfying the conditions required by the above equations, assuming the origin of the $2p \ ^1\Pi_{cd} - 1s \ ^1\Sigma$ system to be the same in the case of the H¹H² molecule as in that of the H¹H¹ molecule, was entirely unsuccessful. However, twelve bands were found in which all the lines satisfy our theoretical equations, if we assume an electronic isotope shift of approximately 135 cm^{-1} . The electronic term value T_e of the $2p \ ^1\Pi_{cd}$ state in the H¹H² molecule is then found to be approximately $100,184 \text{ cm}^{-1}$ units to be compared with $100,049 \text{ cm}^{-1}$ for this same constant in the case of the H¹H¹ molecule.

So large an electronic shift is not, however, unreasonable for two isotopic molecules differing so greatly in mass. A simple calculation shows that the normal mass effect for a system consisting of a single electron and nucleus should give an electronic isotope shift of about 9 cm^{-1} at our observed ν_e for nuclei differing in the ratio of the masses of H¹H¹ and H²H¹. The "specific

effect" of Hughes and Eckart⁴ in the case of the Li⁶ and Li⁷ atoms produces an additional shift of about 3.6 times the normal mass effect for these atoms. Hence if this same ratio holds for the hydrogen molecule, a total electronic shift of about 42 cm^{-1} is to be expected. Of course our observed shift is considerably greater than this, but it appears to be at least of the expected order of magnitude.

By using the observed frequencies of the lines, the origin of each band has been found by means of the calculated value of the rotational energy for each state. For any particular band the calculated origin, as determined from each individual line, was found to be the same to within the experimental error. With the origins thus found, the calculated value of the frequency of each line has been found. Table I gives the observed and calculated wave numbers of lines in each of the twelve bands. Lines marked with an asterisk are known blends. In some cases these blends are very wide on the photographic plate so that the measured values of their wave

⁴ D. S. Hughes and Carl Eckart, Phys. Rev. **36**, 694 (1930).

TABLE I.

Branch	K''	I	Obs. (cm ⁻¹)	Calc. (cm ⁻¹)	$O-C$	Branch	K''	I	Obs. (cm ⁻¹)	Calc. (cm ⁻¹)	$O-C$
(0-2) Band $\nu_0=92,140.1$ cm ⁻¹						(1-5) Band $\nu_0=84,829.2$ cm ⁻¹					
R	0	5	92,182.0	92,182.3	-0.3	Q	1	7	84,799.5	84,799.4	0.1
	1	6	92,193.3	92,193.4	-0.1		2	6	84,747.3	84,746.7	0.6
	2	3	92,167.7	92,169.3	-1.6		3	4	84,668.3*	84,668.3	0.0
	3	2D	92,109.7	92,110.0	-0.3		4	2D	84,562.8	84,565.0	-2.2
P	2	4	91,936.9	91,938.0	-1.1		5	1D	84,436.0	84,437.7	-1.7
	3	8	91,787.2*	91,788.2	-1.0	(2-2) Band $\nu_0=96,068.4$ cm ⁻¹					
	4	6	91,606.7	91,605.9	0.8	R	0	5	96,108.3*	96,106.0	2.3
	5	7	91,388.2*	91,392.4	-4.2		1	5	96,108.3*	96,108.9	-0.6
Q	1	7	92,100.4	92,099.9	0.5	P	2	3	95,861.4	95,861.7	-0.3
	2	8	92,029.0	92,029.1	-0.1		3	3	95,703.9	95,703.7	0.2
	3	4	91,923.0	91,923.4	-0.4	Q	1	5	96,024.5	96,023.8	0.7
	4	8	91,787.2*	91,783.9	3.3		2	2D	95,945.2	95,945.0	0.2
	5	6	91,606.7*	91,611.6	-4.9		3	3	95,826.6	95,827.4	-0.8
(0-3) Band $\nu_0=88,865.1$ cm ⁻¹						(2-3) Band $\nu_0=92,787.6$ cm ⁻¹					
R	0	6	88,908.0	88,907.7	0.3	R	0	7	92,827.8*	92,825.6	2.2
	1	4	88,922.9	88,922.6	0.3		1	7	92,827.8*	92,832.3	-4.5
	2	6	88,908.0	88,905.8	2.5		2	3	92,803.1	92,803.4	-0.3
	3	2	88,857.1	88,857.5	-0.4	P	2	4	92,592.7	92,592.4	0.3
	4	0D	88,779.5	88,778.6	0.9		3	6	92,445.8	92,445.4	0.4
P	2	7	88,671.9*	88,674.5	-2.6	Q	1	8	92,747.9	92,747.2	+0.7
	3	4	88,535.6	88,535.7	-0.1		2	3	92,676.2	92,675.8	0.4
	4	4	88,366.8	88,368.1	-1.3		3	3	92,569.9	92,569.1	0.8
	5	3D	88,168.2	88,172.7	-4.5		4	2D	92,428.4	92,428.6	-0.2
Q	1	7	88,828.7	88,829.1	-0.4		5	3	92,253.6	92,255.0	-1.4
	2	7	88,765.5	88,765.6	-0.1	(2-5) Band $\nu_0=86,741.7$ cm ⁻¹					
	3	7	88,671.9	88,670.9	1.0	R	0	7	86,780.1*	86,780.7	-0.6
	4	2D	88,545.6	88,546.1	-0.5		1	7	86,793.9	86,794.7	-0.8
	5	3	88,390.3	88,391.9	-1.6		2	7	86,780.1*	86,780.5	-0.4
(1-1) Band $\nu_0=97,617.1$ cm ⁻¹							3	7	86,569.2	86,569.5	-0.3
R	1	4	97,660.9	97,659.8	1.1		4	5	87,445.4	86,444.6	0.8
	2	3	97,622.7	97,622.1	0.6		5	3	86,289.2	86,294.0	-4.8
	3	2	97,543.7	97,543.6	0.1		6	2D	86,117.7	86,118.7	-1.0
P	2	4	97,401.9	97,401.0	0.9	Q	1	7	85,926.7?	85,920.3	6.4
	3	3	97,234.9	97,235.9	-1.0		2	7	86,710.3	86,709.6	0.7
Q	1	5	97,571.4	97,570.6	0.8		3	7	86,652.2	86,652.8	-0.6
	2	Hidden by 2nd Lyman Line					4	7	86,569.2	86,568.3	0.9
	3	5	97,364.3	97,365.7	-1.4		5	1D	86,457.6	86,456.9	0.7
							3	3	86,321.0	86,319.5	1.5
(1-3) Band $\nu_0=90,875.4$ cm ⁻¹						(2-6) Band $\nu_0=83,974.4$ cm ⁻¹					
R	0	4	90,915.6	90,915.7	-0.1	R	0	7	84,014.8*	84,013.8	1.0
	1	4D	90,926.6	90,926.5	0.1		1	6	84,031.2	84,031.5	-0.3
	2	2D	90,903.0	90,903.6	-0.5		2	7	84,014.8*	84,024.7	-9.9
P	2	5	90,683.3	90,682.5	0.8		3	5	83,814.6	83,813.7	0.9
	3	4	90,538.8	90,539.6	-0.8	P	2	4	83,698.7	83,699.7	-1.0
	4	4	90,366.7	90,365.9	0.8		3	4	83,557.2	83,563.6	-6.4
	5	3	90,161.5	90,162.5	-1.0	Q	1	7	83,946.7	83,946.4	0.3
Q	1	7	90,837.6	90,837.3	0.3		2	7	83,898.0	83,897.0	1.0
	2	7	90,769.6	90,769.9	-0.3		3	5	83,822.4	83,823.4	-1.0
	3	4	90,668.3	90,669.4	-1.1		4	3	83,725.9	83,726.5	-0.6
	4	4B	90,538.8	90,537.0	1.8	(3-4) Band $\nu_0=91,495.0$ cm ⁻¹					
(1-4) Band $\nu_0=87,768.2$ cm ⁻¹						R	0	5	91,541.3*	91,531.2	10.1
R	0	10	87,807.5*	87,809.0	-1.5		1	5	91,541.3*	91,537.5	3.8
	1	8	87,824.3	87,823.4	0.9		2	3B	91,508.2	91,509.8	-1.6
	2	10	87,807.5*	87,807.9	-0.4		3	3D	91,453.7	91,448.4	5.3
	3	4	87,762.0	87,762.7	-0.6	P	2	2D	91,313.2	91,309.0	4.2
	5	10	87,585.2*	87,585.2	0.0		3	4	91,175.7	91,169.0	6.7
P	2	10	87,585.2*	87,586.8	-1.6		4	2D	91,002.4	90,997.5	4.9
	3	4	87,455.4	87,454.9	0.5		5	2D	90,800.5	90,796.1	4.4
	4	8	87,296.3	87,295.6	0.7	Q	1	7	91,456.2	91,456.3	-0.1
	5	5	87,109.7	87,110.3	-0.6		2	7B	91,388.2	91,388.1	0.1
Q	1	10	87,734.5	87,734.2	0.3		3	5	91,287.1	91,286.3	0.8
	2	10	87,674.9	87,674.2	0.7		4	2D	91,154.3	91,151.9	2.4
	3	10	87,585.2*	87,584.7	0.5	(3-7) Band $\nu_0=83,190.1$ cm ⁻¹					
	4	3	87,467.2	87,466.7	0.5	R	0	5	83,231.5	83,227.7	3.8
	5	1D	87,322.4	87,321.3	1.1		1	6	83,246.6*	83,245.2	1.4
(1-5) Band $\nu_0=84,829.2$ cm ⁻¹							2	6	83,246.6*	83,239.9	6.7
R	0	9	84,871.1*	84,870.5	0.6	P	2	2	83,042.8	83,039.1	3.7
	1	8	84,889.0	84,888.6	0.4		3	3	82,936.2	82,932.4	3.8
	2	8	84,880.7	84,880.4	0.3		4	4	82,809.4*	82,805.2	3.8
	3	2	84,844.4	84,846.2	-1.8	Q	1	7	83,164.0	83,164.0	0.0
P	2	4	84,661.6*	84,659.3	2.3		2	6	83,117.8	83,118.2	0.4
	3	4	84,540.6	84,538.5	2.1		3	4	83,049.8	83,049.7	0.1
	4	3	84,394.2	84,393.9	0.3		4	3	82,961.2	82,959.6	1.6
	5	1	84,225.9	84,226.7	-0.8		5	3	82,847.5	82,848.9	-1.4

numbers have comparatively very large probable error. In other cases the probable error is about 2 cm⁻¹ units or less.

The value of the origins of the bands as given in Table I allow the calculation of a number of the Δ*G_v* values for each of the two states in question. These values are given in Table II.

TABLE II. Δ*G_v* values.

<i>v</i>	For 1 <i>s</i> ¹ Σ State		For 2 <i>p</i> ¹ Π _{cd} State	
	Obs.	Calc.	Obs.	Calc.
1/2			2010.3	2017.6
1 1/2	3466.8*	3453	1912.5	1911.4
2 1/2	3277.8	3278	1814.3*	1804.6
3 1/2	3107.2	3108		
4 1/2	2939.0	2940		
5 1/2	2767.3	2771		
6 1/2	2598.7*	2599		

The probable error of measurement of the Δ*G* values is rather large (about 5 cm⁻¹) since the wave-length interval is larger than the range over which it has been possible to obtain consistent standards. It should be remarked also that the Δ*G* values marked with an asterisk in Table II could not be obtained directly and so may contain the sum of several errors of measurement.

A graphical representation of the Δ*G_v* : *v* data for the two states considered is shown in Fig. 1,

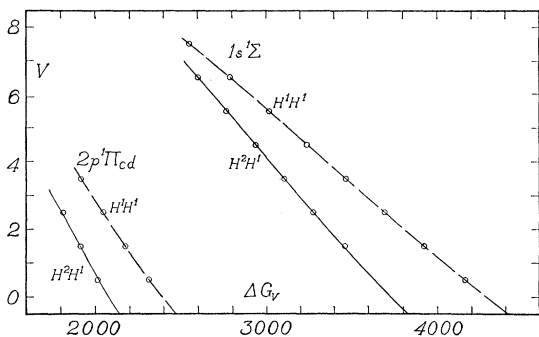


FIG. 1. Graphical representation of the Δ*G_v* : *v* data for the 1*s* ¹Σ and 2*p* ¹Π_{cd} states.

together with the corresponding data for the H¹H¹ molecule. In the case of the H¹H² data the curves drawn are those given by the theoretical Eqs. (5) and (12).

An additional check upon the identification of lines is afforded by a calculation of the term differences Δ*T_K* given by equations of the

following type as suggested by Jenkins and McKellar.⁵

$$\begin{aligned} \Delta T_K &= R^{(1-3)}(K) - R^{(1-4)}(K) \\ &= P^{(1-3)}(K) - P^{(1-4)}(K) \\ &= Q^{(1-3)}(K) - Q^{(1-4)}(K) \\ &= \Delta G_{3\frac{1}{2}}'' - \alpha''(K + \frac{1}{2})^2 + \dots \end{aligned} \quad (13)$$

Accordingly in the cases for which such calculations are possible, Δ*T_K* values have been found and fitted by least squares to equations of the form given by (13). In each of the four cases thus examined the observed values of Δ*T_K* and those calculated by the least squares equations have differences within the probable error of measurement (about 2 cm⁻¹), and the values of Δ*G_v* given by the constant terms of our least squares equations differ by an equally small amount from the Δ*G_v* values obtained by use of the band origins given in Table I.

A typical example of one of these Δ*T_K* : (*K* + 1/2) functions, as obtained from the 1-3 and 1-4 bands, is shown in Fig. 2, together with the same

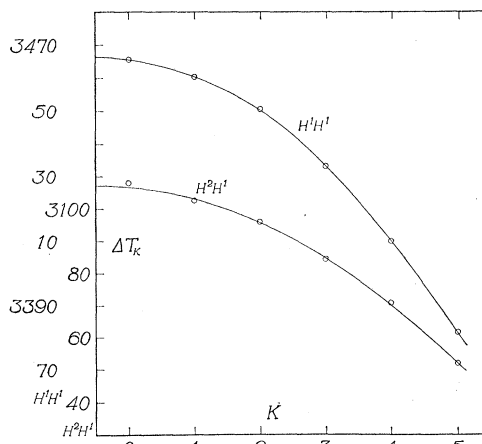


FIG. 2. Typical examples of Δ*T_K* : *K* relations as obtained from 1-3 and 1-4 bands for H¹H¹ and H²H¹.

function as obtained from the data on the H¹H¹ molecule.¹ The curves drawn through the experimental data have been obtained from the least squares equations mentioned above.

The coefficients of (*K* + 1/2)² in these equations

⁵ F. A. Jenkins and Andrew McKellar, Phys. Rev. **42**, 473 (1932).

are the slopes of the $B_v : v$ curve at the particular value of v for which any equation applies. Ordinarily this slope, α , is very nearly constant for low values of v but in the case of the normal state of hydrogen this has been shown¹ not to be true. Due to this fact we cannot determine an experimental value of α_e for this state of the H^1H^2 molecule, although we have the value of α for values of v between $2\frac{1}{2}$ and $5\frac{1}{2}$ inclusive. The ratio α_e^i/α_e , according to the theory of the isotope effect, equals ρ^3 , but as just noted, we cannot unfortunately, obtain this ratio from the data at hand. However, α_v^i/α_v for $v=2\frac{1}{2}$ to $5\frac{1}{2}$, where the $B_v : v$ curve is almost a straight line, is found to be 0.610 as compared with the known $\rho^3=0.650$. The agreement is probably as good as might be expected, and furnishes an independent check upon the correctness of the assignment of lines.

PERTURBATIONS

As has been shown in a former paper¹ there exist a number of perturbations in the levels of the $2p\ ^1\Pi_{cd}$ state of the H^1H^1 molecule. Because of the comparatively small number of bands observed in the present study, not more than a few recognized lines originate on any one particular rotational level. Since any given line may happen to be an unrecognized blend, it is therefore difficult to establish with certainty any perturbations in the H^1H^2 spectrum. However, there is some evidence that a few of these levels may be perturbed. For example, the $K=3$ level of the $v=2$ state appears to have a perturbation

of a few cm^{-1} units. It should be noted that although this level in the H^1H^1 spectrum is perturbed by $-7.4\ \text{cm}^{-1}$ units, one does not, in general, expect the same quantum states to be perturbed in the two systems because the energies are different.

It may be seen at once, however, from Table I that all of the lines of the P and R branches of bands having the $v=3$ state as their initial level are perturbed by about $4.3\ \text{cm}^{-1}$. This apparently is a vibrational perturbation and is very similar to the observed vibrational perturbation of $10.4\ \text{cm}^{-1}$ in the same $v=3$ level of the H^1H^1 molecule. The term value, G_3 , for this level in the H^1H^1 spectrum is $6526\ \text{cm}^{-1}$. In the H^2H^1 spectrum G_3 for the $2p\ ^1\Pi_{cd}$ state is $5734\ \text{cm}^{-1}$ units and $G_4=7453\ \text{cm}^{-1}$. It is very likely that the perturbing level has an isotope shift of an equally appreciable amount so that it is difficult to say whether or not we should expect adjacent levels to be perturbed also. It is seen, however, that the $v=3$ level in the H^2H^1 spectrum is nearer to the perturbed level of the H^1H^1 spectrum than is the $v=4$ state so that even were the perturbing level not shifted, the $v=3$ state should still be affected more than its adjacent levels. It may also be significant that the amount of the perturbation is less in the case of the H^2H^1 molecule than it is for H^1H^1 .

In conclusion the writer wishes to thank Professor Lewis and Dr. MacDonald of the chemistry department for a supply of isotopic hydrogen which has made this investigation possible.