THE ABSORPTION SPECTRA OF SOME HYDRIDE COMPOUNDS IN THE ULTRA-VIOLET

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ABSTRACT

The vapor of the metal was heated to about 1700'C in a carbon tube and hydrogen slowly admitted. Under these conditions several hydride bands were absorbed. The four bands found for *copper* hydride confirm the analysis of Frerichs. Eight silver hydride bands were absorbed which enabled us to form the n_1n_2 scheme. The five gold hydride bands found confirm and extend the work of Bengtsson and three new bands, farther down in the ultra-violet, indicate a new electronic level. Three aluminum hydride bands were absorbed which support the analysis of Eriksson and Hulthen. On nearly all our plates the OH bands at 3064 and 2852 were absorbed. Some bands were found which may be due to the oxides of calcium and silver. We were unable to observe absorption at the CdH and CH bands which are shaded toward the violet.

URING recent years, a rapid advance has been made in the analysis of band spectra, from which important conclusions have been drawn about the structure of molecules. One of the most fundamental conclusions is that the electronic states of the molecules are analogous to those of the atoms, i. e. in band spectra there are terms analogous to the s, p, d, \cdots terms of line spectra. We refer to the works of Birge' and of Mulliken' for a complete discussion of these hypotheses. A large amount of theoretical work in band spectra is based on the analysis of the *emission* bands of N_2 , CO, CO⁺, BO, CN and the large number of MeH compounds. When attempts were made to place all of the emission bands of a molecule on an energy diagram, there has frequently been a feeling of uncertainty in regard to the normal state. In other words—where is the level of zero energy? This question may be best answered by experiments on the excitation of the bands by electronic impacts or the study of the absorption spectrum of the molecule.

While we were studying the absorption spectrum of copper vapor in the visible part of the spectrum, very beautiful absorption bands were observed which were recognized as the well known copper hydride bands. The copper was heated in a small carbon tube to about 1700'C. No attempt was made to exclude the atmosphere from the tube. The vapor pressure of copper at 1500° C is about 1 mm of mercury and of

² R. S. Mulliken, Phys. Rev. 26, 561 (1925).

¹ R. T. Birge, Nature, Feb. 27 (1926).

the water vapor of the atmosphere about 2 cm. If the copper hydride molecule is formed according to the chemical equation,

$Cu+H₂O = CuH+OH$

then we should expect a group of absorption bands due to the OH molecule. Such was found to be the case. The so-called "water vapor" bands at 3064 and 2852 were easily recognized in absorption. They are now attributed to the OH molecule and not, to water vapor. In a recent study of the spectrum of the copper spark under water, Stücklen³ reported that these OH bands were absorbed. The theoretical importance of the hydride bands is due especially to the wide spacing of the lines, resulting from the small inertia moments. This allows one to study the structure of the bands with a quartz spectroscope which is perhaps the only instrument that could be used below 2500A. They also form a large class of band spectra, well known in emission and with a similar structure for all elements in the same group of the periodic table.

We have undertaken a study of several hydride bands in absorption using the same experimental method that has been employed in studying the absorption spectra of metallic vapors in the ultra-violet. This method has been fully described elsewhere.⁴ The metal is placed in a small carbon tube and the tube is heated with an oxy-acetylene torch to the highest temperature possible (about 1700° C). The tube is partly surrounded with concave carbon pieces which utilize the heat of the torch to best advantage and also reduce the loss of heat by radiation. Hydrogen is admitted to the hot tube directly over the surface of the metal. There are two conditions which must be fu1611ed in order to obtain the hydride molecules. The atoms of the metal must be present as indicated by the strong absorption lines of these atoms which are always observed along with the hydride bands. The second condition is perhaps the presence of atomic hydrogen. The intensity of the absorption of the hydride bands is very greatly influenced by the rate of inflow of the hydrogen. We do not know if the atomic hydrogen is produced by a purely thermal dissociation of H_2 or H_2O molecules or if there is a catalytic action due to the hot surface of the metal. As an experimental fact we find that when the hydrogen is rapidly passed through the tube (indicated by bubbling the gas through a wash bottle), the hydride bands are faint. This is partly due to the removal of the metallic atoms by the stream of hydrogen and perhaps

³ H. Stiicklen, Zeits. f. Physik 33, 562 (1925).

⁴ Zumstein, Phys. Rev. 25, 523; 26, 765 (1925).

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also the concentration of the atomic hydrogen is less because of recombination. If on the other hand the hydrogen enters the tube very slowly (about one bubble per second) the hydride bands are also weak although the absorption lines of the metallic atoms are strong. This may be due to the unfavorable influence of the atmospheric oxygen. At some intermediate rate of How of the hydrogen, which depends on the particular metal, the concentration of the hydride molecules is a maximum. The dispersion of our spectroscope is 12A per mm at 5700A and 2.6A per mm at 2500A. The exposures were between 5 and 20 seconds.

We will now mention an experiment which illustrates the advantages of studying hydride spectra in absorption rather than emission. An exposure of 20 minutes was sufficient to give the OH bands at 3064A from the cone of an oxy-hydrogen flame in *emission*. When this flame was placed between our source of light and the spectroscope we obtained these bands in absorption with 5 seconds exposure. Supposing that the *a priori* probabilities for the transitions of the molecule between the excited and the normal states are the same in both directions, the times of exposure in our experiment are very roughly, inversely proportional to the number of OH molecules in both states. Thus the number of OH molecules in an excited state and which would be capable of emit ting the band is a very small fraction of the number in the normal state which are able to absorb it. In fact the general faintness with which the hydride spectra appear in emission is a characteristic property of these bands. Several hours exposure are necessary to photograph them with a large grating. This seems to be due to the instability of the hydride molecule.

We have obtained the absorption spectra of the hydrides of (a) Cu, Ag, Au, Al, 0 and have tried to get those of (b) Cd, Ca, 8, Tl, C, N, Pb, Sn; Regarding the (a) group of elements, we may state that the well known emission spectra of these compounds also appear in absorption. We were also able to extend our knowledge of the term schemes of AgH and AuH leading us to important conclusions about their electronic states. These results will be discussed in detail for the individual molecules. For the (b) group, we found no traces of hydride absorption bands* although for most of these elements the bands are

 $*$ Note on calcium absorption. When we tried to observe the absorption of the CaH bands in the red, we obtained instead the absorption of some of the complicated band groups which appear in emission from the Ca and $CaCl₂$ flame and arc spectra. Thus we obtained the characteristic group of bands at X5934.3—5969 and the intense groups 6179.4-6185 and 6205.7-6211.8. This indicates that these groups belong to a $Ca₂$ molecule or a compound with oxygen or carbon (see Kayser and Konen Handbuch 7, p. 175).

known in emission. This failure may be due to at least three reasons. First: It seems very probable that for most of the (b) group the temperature that could be used was too low to give atomic hydrogen. At high temperatures the vapor was so dense that practically no light could pass through. However for cadmium, carbon and tin the conditions seemed to be favorable for the production of hydride molecules. Second: It is known from experiments on the absorption of tin vapor⁵ that under the conditions of our experiments, we only obtain atoms in excited states which differ from the normal state by $\Delta \nu = 10,000$ cm⁻¹. Also from the present experiments we only find hydride absorption bands from vibrational states less than $5,000$ cm⁻¹ from the normal state. If therefore the final state of the CH and CdH bands is an excited state differing in frequency from the normal state by more than $10,000$ cm⁻¹, then we could not have observed them in absorption. Third: According to a general rule of Birge⁶ and Mecke,⁷ band spectra degraded toward the red are emitted by molecules having a more stable final state and bands degraded towards the violet a more stable initial state. All hydride bands emitted by the elements of the second group $(Mg, Ca, -Zn, Cd, Hg)$ are degraded toward the violet and the structural investigations of these spectra all show a very unstable final state of the molecule. Probably these molecules only remain a very short time in the less excited states and thus their absorption spectra must be more difficult to obtain. This view is strongly supported by the fact that all band spectra of *dipoles* which we found in absorption, CuH, AgH, AuH, AlH, OH and also the absorption bands of $O₂$ are degraded toward the red and thus they fulfill the conditions mentioned above.

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The emission bands of Cu, Ag and Au hydrides^{8,9,10,11} are all shade toward the red and homologous in structure. With the exception of the components due to the isotope effect from the metal, they are of very simple structure containing only one P and one R branch. In what follows, we denote the electronic frequency of a band system by ν_0 , the vibrational quantum numbers of the initial states by n_1 and those of the final states by n_2 (referring to the emission process).

- ⁵ Zumstein, Phys. Rev. 27, 150 (1926).
- ⁶ R. T. Birge, Phys. Rev. 25, 240 (1925}.
- ⁷ R. Mecke, Zeits. f. Physik 32, 833 (1925).
- ⁸ R. Frerichs, Zeits. f. Physik 20, 170 (1923).
- ⁹ E.Bengtsson, Zeits. f. Physik 20, 229 (1923).
- ¹⁰ E. Bengtsson, Arkiv f. Math. Astronomioch Fysik **18,** 27 (1925). ¹¹ E. Bengtsson and E. Svensson, C. R. **180,** 274 (1925).
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Copper hydride. In Table I are given the wave-lengths of the heads of the bands of the CuH spectrum as arranged by Frerichs. In this scheme, the bands 4280 and 4006 of the first row $(n_2=0)$, were very strongly absorbed. Our failure to observe absorption of the 3777 band is due in part to the small dispersion of our quartz spectrograph in this region. The other CuH absorption bands were all observed with a large glass spectrograph. Faint absorption was also observed at the bands 4328 and 4063 of the second row $(n_2 = 1)$. Our experiments thus confirm the arrangement of Frerichs and show that the $n_2=0$ level is the normal state of the CuH molecule. H. Stücklen found a single absorption band at 2240 in the spectrum of the copper spark under water but did not find it in the copper arc in air or hydrogen. We find the same band strongly absorbed in our experiments. It is also re-

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versed in a 100 ampere copper arc in air. This band is probably due to a copper hydride, however the large inertia moment as calculated from the 2240 band shows that the molecule is not the same as the one which absorbs the long wave system. Stücklen has suggested a CuH_2 molecule.

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Silver hydride. We know of two very strong silver hydride bands in emission at λ 3330 and 3358. They have recently been measured and analyzed by Bengtsson and Svensson¹¹ who found that these bands have no common initial or final states. Eder and Valenta in their atlas, give the flame spectrum of AgCl and indicate band heads at 3515, 3540, 3577 and a group of longer wave-length at 3750, 3810, 3900, 4102. We find the bands 3330 and 3358 beautifully developed in absorption and also two faint groups of bands at 3179, 3220 and 3516, 3544, 3583, 3638. The last group is apparently the same as the bands found by Eder and Valenta in emission. From the grouping of the bands we are able to obtain the n_1n_2 scheme of Table II. The figures above the wave-lengths of the heads denote the intensities of the bands in

absorption. We notice a remarkable symmetry in the intensity distribution around the 0 group (3330, 3358) which is characteristic for

TABLE II Bund system of silver hydride (Wave-length of band heads. Numbers above band head denote intensity of absorption and those below, the frequency of the zero line.)

[~] New bands. x Head of this band hid by silver absorption line) 3280

many band spectra $(N_2, AIO, etc.).$ In order to verify this arrangement of the bands, we have analyzed the structure of X3179. In Table III

Silver hydride band λ 3179.4 Wave numbers are reduced to vacuum								
m	R	3179.4 P	Δ_1	Δ_2	3358 Δ_1	3330 Δ_2		
1 $\frac{2}{3}$ 456789 10 11 12 13 14 15 16	x 31407.6 16.6 24.8 30.1 35.6 38.5 41.4 42.8 42.8 41.4 38.5 33.7 28.2 20.8 11.8	31376.5 60.6 44.5 27.6 10.9 292.2 71.4 50.8 29.0 04.6 180.4 54.1 26.9 098.7 69.3	31.1 56.0 80.3 103.5 124.7 146.3 170.0 192.0 213.8 236.8 258.1 279.6 301.3 322.1 342.5	63.1 89.0 113.9 138.9 164.2 187.7 212.4 238.2 262.4 287.3 311.6 335.0 358.9	56.8 80.0 102.6 125.3 147.7 170.0 192.8 \star 236.5 257.9 279.6 301.3 322.4 343.3	63.6 88.8 114.3 139.2 164.2 189.2 214.2 239.2 263.7 288.0 312.2 336.1 359.9		

TABLE III

x not observed.

the wave numbers of the lines are given as we have arranged them in a P and R branch. If the arrangement of Table II is correct, the initial states of 3358 and 3179 should be identical as well as the final states of 3330 and 3179. This comparison can be made by forming the initial and final rotational terms of the bands thus:¹²

$$
P(m) = F(m-1) - f(m)
$$

\n
$$
R(m) = F(m+1) - f(m)
$$

\nfrom which
$$
R(m) - P(m) = F(m+1) - F(m-1) = \Delta_1
$$

\nand
$$
R(m-1) - P(m+1) = f(m+1) - f(m-1) = \Delta_2
$$

Accordingly the Δ_1 values should be the same for 3358 and 3179 and the Δ_2 values for 3330 and 3179. In Table III the Δ_1 and Δ_2 values are given for the bands 3358 and 3330 as calculated from the measurements of Bengtsson and Svensson and we find an agreement within the errors of measurements (approx. 1.0 cm^{-1}). It is to be noted that the emission bands found by Eder and Valenta at 3750, 3810, 3900 also find a place in this scheme.

Other silver bands. We observed a system of absorption bands having double heads at λ 2661.91, 61.46 - 2660.22, 59.90 - 2658.63, 58.18 —2657.19, 56.64. The bands are shaded toward the red and the intensity of the long wave component much greater than that of the short wave one of the doublet. They do not show a fine structure and are perhaps due to an AgO compound as they resemble the CuO bands in the visible. We also observed in absorption a group of nearly equidistant lines (or band heads?) at 2571.78, 69.85, 68.01, 66.02, 64.06, 62.34 but hesitate about the origin of this isolated band or group of bands.

Gold Hydride. The band spectrum of gold hydride in emission has
en studied by Bengtsson.¹⁰ Since the gold vapor seemed to be very been studied by Bengtsson. Since the gold vapor seemed to be very inert toward the atmospheric oxygen and therefore more suitable for study by our method, we have devoted most attention to the gold hydride spectra. Thus we found of the seven bands observed by Bengtsson)4436, 4339, 4068, 3973, 3745, 3652, 3457 only 3973, 3652 and 3457 were absorbed as one would expect. These bands correspond to the final states $n_2=0,1$ in Bengtsson's scheme of the spectrum. We also found two new bands with heads at λ 3298.1 and 3170.0. The wave numbers of the lines of these bands are given in Table IV, columns 1 and 2. In order to find the relation between these bands and those of Bengtsson, we may form their initial and final rotational terms Δ_1 and Δ_2 as we did for silver and compare them with the corresponding Δ values calculated by Bengtsson. These values are collected in Table V. From the agreement between the Δ_2 values of λ 3652, 3457, 3298 and

¹² E. Hulthèn, Ann. d. Physik 71, 43 (1923).

Gold hydride bands (vuc of lines observed) $\mathrm{T}_{\mathrm{ABLE}}$ IV

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* Not observed because of reversal in source of light.

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	Gold hydride bands—I able of Δ values (long wave system).								
	λ 3652			λ 3457		λ 3298		λ 3170	
	$n_1 = 0$	$n_2=0$	$n_1 = 1$	$n_2 = 0$	$n_1 = 2$	$n_2 = 0$	$n_1 = 3$	$n_2 = 0$	
\boldsymbol{m}	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2	
					32.0	.	28.2		
$\frac{2}{3}$					52.0	71.6	48.3	71.5	
			1.1.1.1	.	71.6	99.5	68.5	100.6	
$\frac{4}{5}$.		.		\ast	126.9	89.3	127.7	
$\frac{6}{7}$					113.9	\ast	104.9	158.1	
	\cdots	\cdots	.	.	136.3	184.2	123.2	184.9	
8	.	213.2	.	213.0	*	213.8	143.2	212.2	
9	198.0	240.8	187.4	240.3	176.2	\ast	160.6	240.5	
10	220.3	268.8	208.3	268.4	195.5	270.5	179.0	268.3	
11	243.1	296.6	230.4	296.0	215.6	295.3	196.7	296.8	
12	265.7	324.4	251.7	324.3	234.6	325.2	215.1	324.5	
13	287.9	351.8	273.6	351.7	255.2	352.0	232.2	352.3	
14	309.8	379.3	294.5	378.9	274.3	378.8	249.7	378.5	
15	332.0	405.8	314.1	407.1	294.8	407.4	266.2	406.9	
16	353.5	433.0	334.6	434.2	311.9	434.3	283.2	\cdots	
17	375.8	460.3	354.9	460.8	328.2	\cdots	\cdots	.	
18	396.6	487.5	.	487.2	.	.	.		
19	417.5	513.4	.						
20	438.3	539.4	.	.	\cdots	.	.	.	
21	458.3	565.4	ره د د د د						
22	478.3	591.1			.				
23	498.1	616.0			\cdots		.		
24	517.1	640.9	.	\cdots	\mathbf{r} , and \mathbf{r} , and \mathbf{r}	\cdots	α , and α , and	.	

 ${\bf Table~V~A} \label{eq:subd}$ Gold hydride bands—Table of Δ values (long wave system)

TABLE V B

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Gold hydride bands—Table of Δ values (short wave system).

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3170, we conclude that these four bands have the same final state $n_2=0$. Both from their Δ_1 values and the distribution of the 0 lines $(\nu_0$ values are given in Table VI), we conclude that they belong to a set of vibrational states $n_1 = 0, 1, 2, 3$.

Farther out in the ultra-violet, we found three new bands at λ 2773.9, 2612.3 and 2511.7 which have the same structure as the bands of Bengtsson. Their lines aregiven in columns 3, 4, 5 of Table IU. Comparing the Δ values of these bands with those of the Bengtsson bands (Table V B) we find that 2612.3 and 2511.7 belong to the state $n_2 = 0$ and 2773.3 to $n_2 = 1$. From their Δ_1 values we conclude that 2773.3 and 2612.3 have the same initial state. This system is widely separated from the long wave system $(\Delta \nu \text{ approx. } 10,000 \text{ cm}^{-1})$. We therefore conclude that it belong to a new excited electronic level of the AuH molecule $(n_1' = 0, 1).$

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Band systems of gold hydride (Wave-lengths of band heads. Underlined bands were absorbed. Numbers below band heads are frequencies of zero lines.)

[~] New bands, not found in emission.

In Fig. 1 we have compared our results of the CuH, AgH and AuH absorption spectra, showing the electronic levels. If we consider the homologous structure of the spectra of these compounds, we may expect to find a new state in CuH and AgH corresponding to the second excited state in AuH. In spite of several attempts we did not find a new band system for either of these hydrides. It seems certain that such systems exist and that they could be found by improving the experimental methods.

The electronic levels of gold hydride, Fig. 1, approximately fit a Rydberg formula. From the analysis of the structure of the bands, we find that the rotational terms can be approximately represented by Kratzer's formula:¹³

$$
W_r^m = B^n(m - \epsilon)^2 + 2\delta(m - \epsilon) + \cdots
$$

¹³ A. Kratzer Ann. d. Physik 71, 72 (1923).

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 ϵ is 1/2 for all the states of CuH, AgH and AuH. According to the theory,¹⁴ ϵ is closely connected with the electronic system of the molecule so that its value in some way indicates the nature of the electronic terms. It therefore seems probable that all the electronic levels indicated in Fig. 1 are s terms. This violates the selection principle for line spectra; however Birge' has pointed out that the selection principle may not hold so rigidly in band spectra.

Fig. 1. Electronic energy levels in CuH, AgH, and AuH.

There is a close parallel between the nuclear distances (r) and the vibrational frequencies (ω) of the normal and the excited states of AuH. We have calculated from Tables V and VI that

> $r_2 = 1.56 \times 10^{-8}$ cm, $\omega_2 = 2256$ cm⁻¹ $r_1 = 1.72 \times 10^{-8}$ cm, $\omega_1 = 1626$ cm⁻¹ $r_1' = 1.74 \times 10^{-8}$ cm, $\omega_1' \sim 1600$ cm⁻¹

This shows that the molecule is most stable in the normal state. The emitting electron, when in the normal state, therefore plays an important part in binding the nucleii to the electron system of the molecule. In the excited states, this binding effect is decreased which is additional evidence that we are dealing with s terms. For ZnH, CdH, and HgH the electron in the excited states moves in $2p_{1,2}$ orbits, and makes the excited molecule more stable than the normal molecule.

Aluminum hydride. These bands have recently been studied in Aluminum hydride. I hese bands have recently been studied is
emission and analyzed by Eriksson and Hulthen.¹⁵ Four bands hav ing P , Q and R branches were arranged thus:

¹⁴ R.S. Mulliken, Proc. Natl. Acad. Sci. 12, 144 (1926.)

¹⁵ G. Eriksson and E. Hulthèn, Zeits. f. Physik 34, 775 (1925).

They noted that the λ 4241 band was reversed in the arc and also a very curious effect. The series of lines of the bands become remarkably broad and vanish at a certain rotational state of the excited molecule $(m=24$ for $n_1=0$ and $m=13$ for $n_1=1$). The three absorption bands 4241, 4067, 4354 were strongly absorbed and showed the same effect.

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