THE SPECTRUM OF GOLD CHLORIDE

By W. F. C. Ferguson

Abstract

The spectrum of gold chloride vapor excited by streaming active nitrogen was photographed. It was found to consist of 43 bands comprising, for each isotope of AuCl, two intermingled systems in the green region. All the bands are shaded toward the red. No other bands were found between λλ7000 – 2000. The band heads of each system were measured, and equations are given representing their positions. Agreement with theory was found for the isotopic displacement of the band heads due to the chlorine isotopes. The vibrational intensity distribution agrees with that theoretically expected from the observed relative values of the initial and final vibrational frequencies. Attempts to excite spectra of gold bromide and iodide in a similar manner were without success.

General Procedure

VAPOR from gold trichloride ($AuCl_3$) was introduced into a stream of active nitrogen after the method originated by Strutt and Fowler,[1] as recently used by Mulliken.[2] The spectrum thus excited was examined in the region λλ7000 – 2000 and, except for certain atomic lines, was found to consist only of a number of bands in the green. These bands are all shaded toward the red. A reproduction of the bands is given in Fig. 1.

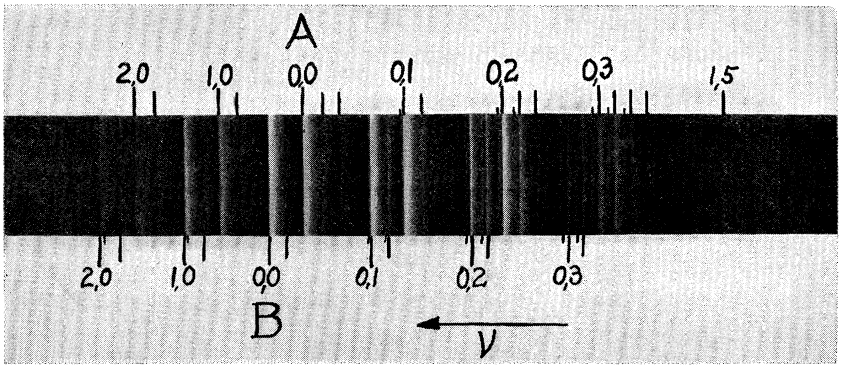

Fig. 1. Spectrum of gold chloride excited by active nitrogen. Bands of the *A* system are marked by vertical lines above; bands of the *B* system are marked below. Each $AuCl^{35}$ head is indicated by a long line; each $AuCl^{37}$ head by a short line.

The photograph used for measurement was made with a quartz spectrograph giving a dispersion in the green of about 28A per mm. An Eastman astronomical green sensitive plate was used, with an exposure of about three hours. The measurements of the band heads are given in Tables I and II.

[1] R. J. Strutt and A. Fowler, Proc. Roy. Soc. **A86,** 105 (1911).
[2] R. S. Mulliken, Phys. Rev. **26,** 1 (1925).

TABLE I. *A Bands.* Column n' n'' gives the vibrational quantum numbers; O–C, observed minus calculated values of wave number, calculated values being obtained from the formulas given in this paper.

		AuCl^{35} heads				AuCl^{37} heads			
n'	n''	Int.	λ (I. A.)	Wave-no.	O−C	Int.	λ (I. A.)	Wave-no.	O−C
2	0	1	5075.0	19699.	1				
3	1	00	94.1	625.	−1				
1	0	4	5155.90	389.9	1				
2	1	000	75.6	316.	−2				
0	0	5	5240.02	078.6	0				
1	1	0	60.6	004.	−5				
2	2	0	78.4	18940.	−1				
0	1	5	5346.65	698.1	0	0	5344.4	18706.	−2
1	2	0	65.6	632.	1				
0	2	4	5456.76	320.8	0	1	5451.1	340.	1
1	3	2	76.01	256.4	0	0	70.1	276.	0
2	4	0	95.4	192.	−1				
0	3	2	5570.4	17947.	1	0	5562.1	17974.	1
1	4	2	90.20	883.5	0	0	81.6	911.	−1
2	5	1	5609.5	822.	−1	00	5601.6	847.	−6
3	6	00	30.0	757.	−7				
1	5	00	5706.8	518.	4				

TABLE II. *B bands.*

		AuCl^{35} heads				AuCl^{37} heads			
n'	n''	Int.	λ (I. A.)	Wave-no.	O−C	Int.	λ (I. A.)	Wave-no.	O−C
2	0	1	5041.74	19828.9	0	1	5046.6	19810.	−5
3	1	0	61.4	752.	−4				
1	0	4	5121.95	518.4	0	00	5123.4	513.	1
2	1	0	40.8	447.	−2				
0	0	5	5205.53	205.0	0				
1	1	000	23.2	140.	2				
0	1	5	5310.61	18825.0	0	1	5308.24	18833.4	−1
1	2	1	29.0	760.	−1	000	26.7	768.	−4
0	2	3	5419.43	447.	0	1	5414.2	465.	0
1	3	2	37.56	385.5	0	0	31.8	405.	0
0	3	1	5531.67	072.8	1	00	5523.0	101.	2
1	4	1	49.89	013.4	0	0	41.1	042.	1

In addition to the bands, the gold lines at λλ4792.6, 3122.8, 3029.2, 2748.3, 2776.0, 2641.5, 2428.0, and 2352.7 appeared on the plates.

ANALYSIS OF BANDS

From its structure, the observed band spectrum is obviously that of a diatomic molecule, presumably AuCl. Most of the strong heads are accompanied each by a closely adjacent weak head (cf. Fig. 1) the two heads being

interpreted as due to $AuCl^{35}$ (stronger) and $AuCl^{37}$ (weaker). It was found possible to arrange all the observed $AuCl^{35}$ bands in two systems, which will be called A and B. All observed bands are represented within experimental error by the following formulas. The formulas for $AuCl^{35}$ were obtained directly from the data, and those for $AuCl^{37}$ were then calculated from theory using the appropriate value (see below) of the isotopic coefficient ρ. The equations are given as functions of $n+\frac{1}{2}$, $(n=0, 1, 2 \ldots)$ because this is required by the new quantum mechanics and has also been shown to be necessary experimentally for certain molecules,[3] although not required by the experimental data in the present case.

$$A\begin{cases}\text{AuCl}^{35}\text{: } \nu=19113.8+312.0(n'+\frac{1}{2})-382.8(n''+\frac{1}{2})-0.70(n'+\frac{1}{2})^2+1.30(n''+\frac{1}{2})^2\\ \text{AuCl}^{37}\text{: } \nu=19113.8+304.8(n'+\frac{1}{2})-373.9(n''+\frac{1}{2})-0.67(n'+\frac{1}{2})^2+1.24(n''+\frac{1}{2})^2\end{cases}$$

$$B\begin{cases}\text{AuCl}^{35}\text{: } \nu=19238.3+316.3(n'+\frac{1}{2})-382.8(n''+\frac{1}{2})-1.45(n'+\frac{1}{2})^2+1.30(n''+\frac{1}{2})^2\\ \text{AuCl}^{37}\text{: } \nu=19238.3+309.0(n'+\frac{1}{2})-373.9(n''+\frac{1}{2})-1.38(n'+\frac{1}{2})^2+1.24(n''+\frac{1}{2})^2\end{cases}$$

Isotope Effect

The theoretical isotopic coefficient[4] ρ has the value 0.9768 for $AuCl^{37}$ as compared with $AuCl^{35}$. As already noted above, the equations for the $AuCl^{37}$ heads were calculated from those experimentally determined for

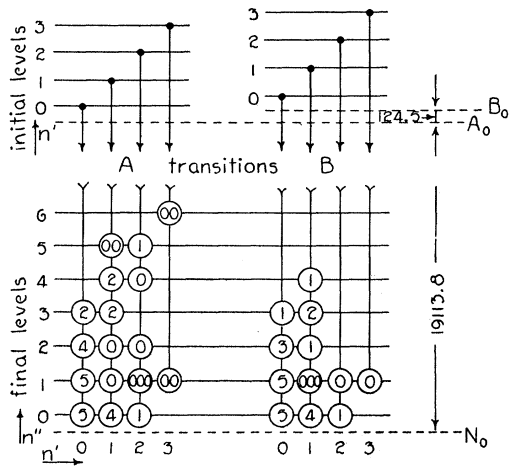

Fig. 2. Energy-levels and transitions in AuCl. N_0 represents the final (normal), A_0 and B_0 the excited electronic levels. Vibrational levels are drawn to scale (indicated by the separation of A_0 and B_0).

$AuCl^{35}$. The agreement of the observed $AuCl^{37}$ heads with these equations (Tables I and II) confirms the identification of the emitting molecule as AuCl. The value of ρ for the isotopes (197, 199) of gold is 0.9992 for AuCl, too near unity to permit their resolution with the dispersion here employed.

[3] R. S. Mulliken, Phys. Rev. **25**, 259 (1925); F. A. Jenkins, Proc. Nat. Acad. Sci. **13**, 496 (1927).

[4] R. S. Mulliken, Phys. Rev. **25**, 119 (1925).

Energy Levels

The identity of the coefficients of the terms in n'' for systems A and B shows that these have the same final electronic state. This is presumably the normal state of the AuCl molecule.

The energy-level diagram (Fig. 2) shows the observed electronic and vibrational levels as determined by this analysis for AuCl.[35]

Intensities

Relative intensities in each system are indicated by numbers in the small circles of Fig. 2. In each system the maximum is near the origin, and the intensity varies in accordance with the theory proposed by Condon.[5] In both the AuCl systems the ratio of final to initial vibrational frequencies is rather far from unity. As is predicted by Condon's theory for such a case, a curve drawn through the strong bands on the $n'n''$ diagram would have a rather wide-open parabolic form.

An attempt was made to excite the bromide and also the iodide of gold by this method, but with no success.

To Professor R. S. Mulliken for his suggestions and guidance during the course of this work the writer is deeply grateful.

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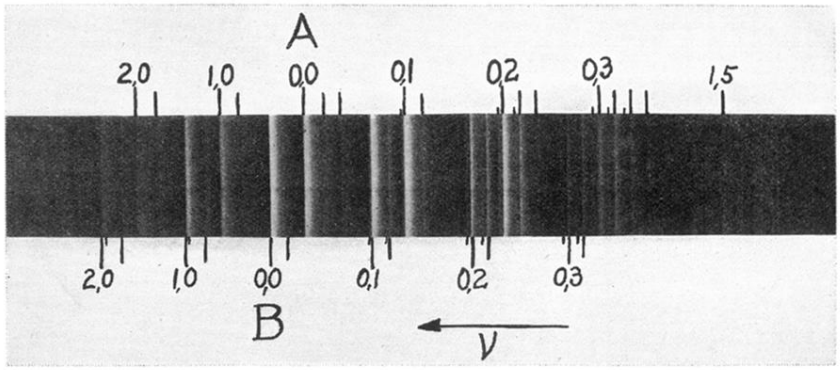
[5] E. U. Condon, Phys. Rev. **28**, 1182 (1926).



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