be chosen for study. The other three are far more serious in an arc than in a low pressure source. In locating maxima, overlapping may be more troublesome than in locating intersections. Inhomogeneity of temperature, which is to be expected only in sources at comparatively high pressure, clearly invalidates any assignment of rotational temperature. Self-absorption and self-reversal would not be expected to change the position of the maximum or the intersections, although these processes result in pronounced deviations from linearity in the intensity factor graphs. The layer of gas between the discharge and the window of the tube in our experiments was at a pressure of about 10^{-4} atmosphere, and about 10 cm long, hence no flattening of line contours was obtained on our plates.

A systematic study of rotational temperatures in comparison with temperatures measured by conventional means has been carried out by Thompson[19] for a low voltage arc in nitrogen, with respect to the negative nitrogen band at 3914A. He found rotational temperatures 300° higher than furnace temperatures of 600°K, and at higher furnace temperatures the discrepancy was less. It is clear from our data that the electrodeless discharge is a much cooler source than the low voltage arc, since the rotational temperature is within about 90° of the furnace temperatures of 353° and 383°K, and substantially equal to the furnace temperature at about 640°K. Although Thompson estimates the error of the determinations using the intensity factor graphs at 2 percent, his plotted points of differences between rotational and furnace temperatures show fluctuations as high as 20 percent. He offers no explanation for these fluctuations.

A possible use of band lines as calibration marks for photometry of spectrum plates is suggested by the great range of line intensities in a band, and the apparent reproducibility of the intensities under controlled temperature conditions. Our studies are not extensive enough to furnish sufficient evidence on this point, but the distributions obtained so far are remarkably consistent.

ACKNOWLEDGMENTS

The authors acknowledge with thanks the aid of Mr. George E. Hansche in obtaining some of the spectra studied, and of Mr. H. W. Speicher in undertaking preliminary experiments. We are grateful also for the assistance of Professor J. B. Green in obtaining the spectrum photographs.

DECEMBER 1, 1937 PHYSICAL REVIEW VOLUME 52

Band Spectrum of TiCl

KENNETH R. MORE,* *Sloane Physics Laboratory, Yale University, New Haven, Connecticut*

AND

ALICE H. PARKER, *Pupin Physics Laboratory, Columbia University, New York, N. Y.*

(Received September 13, 1937)

The emission spectrum of TiCl has been excited by both high frequency and low frequency discharges through a continuous flow of $TiCl_4$ vapor in a discharge tube. The spectrum consists of one strong group of bands and several weaker groups, all degraded to shorter wave-lengths. The strong group occurs between 4200 and 4100A and the weak groups between 4100 and 3700A. The strong group is attributed to a transition between doublet electronic levels. The analysis of this system gives the values $\nu_e = 23820.0$ cm^{-1}, $\omega' = 503.4$ cm^{-1}, $x'\omega' = 2.5$ cm^{-1}, $\omega'' = 456.4$ cm^{-1}, $x''\omega'' = 6.3$ cm^{-1}.

INTRODUCTION

FOWLER,[1] in 1907, reported three band heads at 4199.5, 4192.7, and 4188.0A which he attributed to the TiCl molecule. This spectrum has been rephotographed and examined in an attempt to make a vibrational analysis. The spectrum was found to extend from 3700 to 4200A, with the strongest bands between 4150 and

---

* Sterling Fellow.

[1] A. Fowler, Proc. Roy. Soc. A79, 509 (1907).

Table I. *Wave numbers and intensities of TiCl band heads.*

v',v''	P_1 or P_2					
0,0	23805.6(1)*	23844.5(10)	23864.8(4)	23871.3(8)	23890.8(6)	23906.4(5)
1,1		23899.1(9)	23920.5(4)	23930.8(8)	23946.3(5)	23965.4(3)
2,2		23961.3(9)	23983.4(4)	23995.6(7)	24013.2(5)	24033.7(*bl*)
3,3		24030.1(6)	24057.4(*bl*)	24069.5(5)	24090.0(*bl*)	24112.7(1)
4,4		24106.8(3)	24136.3(3)	24147.4(2)	24178.3(1)	24206.3(0)
5,5		24191.7(*bl*)	24225.2(0)	24233.4(0)	24274.6(0)	
1,0		24342.8(3)				
2,1		24392.3(2)				

* The intensities given in brackets after the wave numbers are visual estimates on a scale of 0–10. Heads which are blended with atomic lines are marked "*bl.*"

4200A. The head at 4192.7A reported by Fowler was the strongest one observed.

Experimental

The spectrum attributed to TiCl was excited by two methods. One was the passage of a low frequency discharge between electrodes which were approximately one centimeter apart. The discharge took place in a flask containing $TiCl_4$ at its room temperature vapor pressure. One electrode was a copper cup containing titanium metal. The other was a water-cooled copper rod. The electric power was supplied by a 1 kva Thordarson transformer. The second method used to excite the bands was the passage of a high frequency discharge through a tube containing $TiCl_4$ vapor at a suitable pressure. The discharge tube, which was of the external electrode type, was one centimeter in diameter. The $TiCl_4$ vapor was pumped through the discharge tube from a side tube containing liquid $TiCl_4$. The pressure in the discharge was controlled by varying the temperature of the liquid $TiCl_4$. A temperature of 10°C was found to be satisfactory. The high frequency discharge was much more intense than the low frequency one.

The spectrum excited with the low frequency source was photographed in the second order of a 21-foot grating giving a dispersion of 1.3A per mm, while that excited by the high frequency source was photographed in the third order of a 21-foot grating in a stigmatic mounting. The latter instrument gave a dispersion of 1.5A per mm. In the former case exposures of from 2 to 24 hours were taken, while in the latter 40 minute to 3 hour exposures were sufficient. Iron arc comparison spectra were recorded on all plates.

Table II. *$\Delta G(v)$ values for the P_1 or P_2 heads.*

$\Delta G'(v)$	$v-v$	$\Delta G''(v)$
498.3	0−1	443.7
493.2	1−2	431.0

Table III. *Isotopic bands.*

√ Ti^{48}Cl^{35}	√ Ti^{48}Cl^{37}	√ (obs.)	√ (calc.)
23961.3 (9)*	23958.8 (1)	2.5	2.2
23983.4 (4)	23980.0 (0)	3.4	2.6
24342.8 (3)	24334.9 (0)	7.9	8.3

Titanium arc spectra were also recorded on many plates. These were used for the identification of the titanium lines which were excited in the discharge.

Analysis

The intense group of bands between 4150 and 4200A can be arranged into six overlapping sequences of rather closely spaced band heads. The wave numbers of the heads are given in Table I. The high intensity of this group relative to the others suggests that the sequences mentioned arise from transitions for which $\Delta v=0$. Since the electronic terms and coupling cases are not known, symbols are not assigned to the different branches. It is probable, however, that the strongest sequence, because of its position relative to the others, consists of P_1 or P_2 heads.

The bands of the $\Delta v=+1$ sequence are fairly weak, while those of the $\Delta v=-1$ sequence are not observed. It is probable that many weak bands of these sequences are masked by strong titanium lines. The weakness of the bands for $\Delta v=\pm 1$ is consistent with the Franck-Condon principle because the difference between ω' and ω'' is relatively small. Band heads which are attributed to the $\Delta v=+1$ sequence of P_1 or P_2 heads are given in Table I. The $\Delta G(v)$ values for the P_1 or P_2 heads are given in Table II. From the values given in Tables I and II the following equation is deduced for the heads of the P_1 or P_2 branches:

$$\nu=23820.0+[503.4(v'+\tfrac{1}{2})-2.5(v'+\tfrac{1}{2})^2]\\ -[456.4(v''+\tfrac{1}{2})-6.3(v''+\tfrac{1}{2})^2].$$

The wave numbers of the last three heads of the $\Delta v=0$ sequence are not used in determining the constants of this equation. It is therefore of importance that the values calculated from the equation agree well with the observed wave numbers.

An interpolation between the ω'' values 535 cm^{-1} and 353 cm^{-1} for the monochlorides of Si[2] and Sn,[3] elements which are respectively above and below Ti in the periodic table, indicates that ω'' for TiCl should be in the range 400 to 490 cm^{-1}. In addition there is evidence that ω'' usually changes slowly in going from compounds of one element to the next as a given electron shell is being built up. The frequencies for the chlorides of Ni,[4] and Cu[5] are respectively 420 and 417 cm^{-1}. Thus a value of the order of 440 cm^{-1} is reasonable for ω'' of TiCl. This leads to a value of about 500 cm^{-1} for ω' because of the observed sequence intervals. Such a value of ω' supports the identification of the bands assigned to the $\Delta v=+1$ sequence because no other bands are observed with a separation from the $\Delta v=0$ heads of less than 700 cm^{-1}.

The bands which have been discussed above are attributed to the molecule $Ti^{48}Cl^{35}$. Since the abundance ratio of the chlorine isotopes is $Cl^{35}:Cl^{37}=100:31.4$, the intensity of the bands due to the $Ti^{48}Cl^{37}$ molecule should be 31 percent of the intensity of the corresponding bands due to the $Ti^{48}Cl^{35}$ molecule. The displacement coefficient $(\rho-1)$ is -0.0158. Band heads which can be attributed to the isotopic molecule are given in Table III, together with the corresponding heads due to the main molecule, the observed and the calculated isotope displacements. Only a few heads due to the isotopic molecule are observed because of the low intensity of many of the bands which are far enough from the system origin for the isotope effect to be appreciable, and because of the masking of weak isotopic bands by stronger bands or by atomic lines.

In addition to the bands which have already been discussed, bands are observed in the regions 4050 to 4000A, 3935 to 3840A, and 3750 to 3720A. These bands, which are all much weaker than the heads of the 4192A system, are not sufficiently well developed for purposes of analysis. It is probable that most of the bands observed are to be attributed to TiCl because the high intensity of the atomic titanium and chlorine lines indicates that a considerable amount of complete dissociation of the $TiCl_4$ occurs in the discharge. It is probable that under such conditions the spectrum of diatomic TiCl would be excited in preference to the spectra of polyatomic fragments formed by the partial dissociation of the $TiCl_4$. This interpretation indicates the presence of more than one excited electronic state of the TiCl molecule.

The ground state of the TiCl molecule is probably a doublet state formed by the combination of the $3d^2\ {}^3F$ ground state of Ti I and the $3p^5\ {}^2P$ ground state of Cl I. The Λ value of the terms can be 0, 1, 2, 3, or 4. The excited states are probably also doublets, built by the combination of excited triplet and singlet states of Ti I with the ground state of Cl I. Again states of high Λ values are possible.

The intensity distribution among the branches of the band group at 4192A furnishes some evidence about the type of electronic transition. The strongest sequence is the one beginning with the band at 4192A. Only the weak sequence beginning at 4199A lies farther to the red. It thus seems necessary to interpret the 4192 sequence as being P_1 or P_2 heads and the 4199 sequence as being weak satellite heads. Even though the other sequences cannot be assigned it is evident that the Q heads are not as strong as the P heads. This suggests that the transitions are probably ${}^2\Pi\rightarrow{}^2\Delta$, or ${}^2\Delta\rightarrow{}^2\Phi$.

---

[2] W. Jevons, Proc. Phys. Soc. **48**, 563 (1936).

[3] W. Jevons, Proc. Roy. Soc. **A110**, 365 (1926); W. F. C. Ferguson, Phys. Rev. **32**, 607 (1928).

[4] K. R. More, Phys. Rev. **51**, 1019 (1937).

[5] R. Ritschl, Zeits. f. Physik **42**, 172 (1927).