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Extension of the Spectrum of AgCl

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The absorption of AgCl vapor below λ2500 has been investigated with high dispersion. A new band system obeying the formula

$$\nu_{\text{head}}=43{,}525.4+294.1u'-1.70u'^2-342.8u''+2.14u''^2$$

has been found, and a fragment of another similar system. Strong continuous absorption is observed at higher pressures.

It has been suggested by Mulliken[1] from a study of the electronic structures of the silver halides AgX that these molecules should show further absorption bands and continue below λ2500. The known spectrum of AgCl consists[2] of a single strong system in the region λλ3100–3400, designated by Mulliken $B \leftarrow N$. The positions and characteristics of the states above B are difficult to predict because of the strong interaction which is expected between them. The present investigation shows the existence of an extensive system covering the region λλ2100–2300, as well as part of another below λ2200 and a continuum at still shorter wave-lengths. Some of the characteristics of these transitions are in excellent agreement with Mulliken's predictions.

In exploring the absorption spectrum of AgCl vaporized in the carbon-tube furnace (see preceding article), we found on our low dispersion plates a set of rather faint bands below λ2300. These could only be seen when the temperature of the furnace was held between the rather narrow limits 1150 to 1220°C. At higher temperatures the system is blotted out by a continuous spectrum which extends to eventually join the absorption by the $B \leftarrow N$ system above 1700°C. The new 30,000-line/in. aluminum grating now in our 21-foot mounting proved admirably suited to the investigation of this region. With a hydrogen lamp of the conventional type, having a capillary of $2\frac{1}{2}$ mm internal diameter and carrying a current of 0.4 amp., it was possible to photograph the continuum on Schumann plates down to the beginning of the O_2 absorption bands at λ1950 with an exposure of $\frac{1}{2}$ hour. By carefully adjusting the current in the furnace, satisfactory plates of the AgCl absorption were obtained showing sharp bands as far as λ2100, below which they are masked by the continuous absorption.

The bands are all degraded toward the red and have a fairly open structure with the heads not pronounced. An enlargement of the 1,1 and 2,2 bands is shown in Fig. 2(*d*) of the preceding article. Resolution is not sufficient for an analysis by the combination principle. Measurements of the band heads were made against iron lines, using the new wave-lengths determined by Meggers and Humphreys.[3] The results are given in Table I, which includes all measured bands. Because of the indistinct character of the heads, some of the values are in error by several wave numbers. Many of the fainter heads appeared only as a rise in intensity of the structure lines from the preceding band, and the settings on these had to be made in a somewhat arbitrary manner.

The assignment of vibrational quantum numbers for the main system is definite. It is confirmed by the isotope effect, which, however, is not as clearly marked as in the longer wave-length system.[2] Each band has four heads, the pairs due to $Ag^{107,\,109}$ having about one-ninth the separation of those due to $Cl^{35,\,37}$. On the long wave-length side of the origin the Ag pairs were clearly resolved for the stronger bands, and the measurements of Table I refer to the first strong head, $Ag^{109}Cl^{35}$. On the short wave-length side the Ag pairs could not be separated, and the heads

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[1] R. S. Mulliken, Phys. Rev. **51**, 310 (1937).

[2] B. A. Brice, Phys. Rev. **35**, 960 (1930).

[3] W. F. Meggers and C. J. Humphreys, Nat. Bur. Stand. J. Research **18**, 543 (1937).

TABLE I. *Band heads of* $AgCl^{35}$. *The bands are shaded toward long wave-lengths.*

v' \ v''	0	1	2	3	4	5	6	7	8	9
0		43,162.0	42,823.8	42,487.7	42,154.1	41,823.0	41,490.4	41,168.0		
1		43,453.5	43,115.2	42,778.1	42,450.1			41,466.9	41,135.4	40,800.7
2	44,084.1	43,744.9	43,405.5			42,406.4	42,073.0			
3	44,372.8	44,032.1	43,693.1		43,025.3	42,693.1				
4	44,660.1	44,321.6		43,654.3	43,315.7					
5	44,945.6	44,608.0		43,930.4			42,935.3			
6	45,231.3									
7	45,512.7									
8	45,794.2									
9	46,070.5									
10	46,347.3									
11		46,283.2								
v' \ $v''\pm1$	5	6	7	8	9					
0	47,466.4	47,138.8	46,814.2	46,490.2	46,165.6					
1		47,429.4	47,101.5							

due to Cl^{37} could only be measured with difficulty. Hence for these bands the measurements represent $Ag^{107}Cl^{35}$ heads. No correction has been made for this difference in view of the necessarily approximate character of many of the measurements. The measured isotope shifts are compared in Table II with their calculated values. The agreement is sufficient to establish the vibrational numbering and the carrier of the bands.

The band heads of the main system in Table I are represented by the equation

$$\nu = 43{,}525.4 + 294.1u' - 1.70u'^2 - 342.8u'' + 2.14u''^2,$$

where $u = v + \frac{1}{2}$. The constants for the vibrational energy G'' agree with those given by Brice[2] for the system $B \leftarrow N$, so that there can be no question that the two systems have the lower state N in common.

The vibrational intensity distribution is of the wide parabola type required by the Franck-Condon principle when there is a large change in moment of inertia between the initial and final states. The 0,0 band is entirely absent, and the intensity maxima in the $v'=0$ and $v''=0$ progressions come at $v''=4$ and $v'=6$, respectively. A rather marked secondary parabola appears below the main one.

In the lower part of Table I are given the data for seven additional hands which overlap the short wave end of the above system, and which apparently form part of a second system. The spacing and appearance of these bands are very similar to the above, and they probably form parts of two progressions $v'=0$ and 1, as indicated by the tentative assignment of quantum numbers in Table I. The assignments of v'' were made chiefly on the basis of the $\Delta G''$ values. Also there is a faint band 32.7 cm^{-1} to the violet of 0,6, which is probably the corresponding Cl^{37} head since the shift has about the right magnitude if the system origin is at about 48,800 cm^{-1}. If this system has a vibrational structure similar to the above, one could not observe bands of higher frequency than 0,5, because they are masked by the continuous absorption.

As regards the intensities of these systems as a whole, they are evidently much fainter than the

TABLE II. *Isotope shifts.*

v',v''	$\Delta\nu$(obs.)	$\Delta\nu$(calc.)
$Ag^{107}Cl^{35}-Ag^{107}Cl^{37}$ $\rho-1=-0.020577$		
6,0	29.1	34.30
5,0	26.0	28.72
4,0	22.5	23.01
$Ag^{109}Cl^{37}-Ag^{109}Cl^{35}$ $\rho-1=-0.020672$		
0,3	22.0	21.23
0,4	28.3	27.97
0,5	36.4	34.60
0,6	50.8	41.18
$Ag^{109}Cl^{35}-Ag^{107}Cl^{35}$ $\rho-1=-0.002264$		
1,3	2.1	1.67
0,4	2.9	3.06
0,5	3.8	3.79
1,8	5.4	5.26

$B \leftarrow N$ system. The latter is well developed at a furnace temperature of 1080°C, while no trace of our present bands is seen below 1150°C. The continuum has stronger absorption, as it begins to appear at the ultraviolet end at temperatures slightly below 1080°C.

Mulliken[1] predicts two transitions for this region, $V \leftarrow N$ and $Q_0 \leftarrow N$, of which the latter should probably give a continuum. The extended system described above is probably to be identified with $V \leftarrow N$. The bands are single-headed, as expected, and from the vibrational intensity distribution it can be concluded that r_e' is considerably greater than r_e''. This is also attested by some measurements of the rotational structure of the 1,1 band. A distinct series originating at the head could be measured, and followed the equation

$$\nu = 43{,}451.34 - 0.022M^2.$$

Thirty consecutive lines ($M = 16$ to 46) were measured. The value of $B' - B''$ is therefore -0.022, while B'' itself is of the order of 0.121 cm^{-1} according to Badger's relation I.[4] The most striking characteristic of our state V, however, is the fact that although r_e is much greater than in the normal state, ω_e is only very slightly less. Exactly the opposite behavior is observed in state B, which has nearly the same r_e as the normal state, but an ω_e which is even less than that we find for state V. These peculiarities of these states agree with the strong interaction between the various curves postulated by Mulliken.

It seems unlikely that our second system is $Q_0 \leftarrow N$, because it is so similar to $V \leftarrow N$. The strength of the continuum does not seem too great to ascribe it to $Q_0 \leftarrow N$.

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[4] R. M. Badger, J. Chem. Phys. 2, 128 (1930).

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Temperature Determinations from Band Spectral Data

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A method of interpreting intensity distributions of lines in a band for determining the temperature of the emitter has been worked out which is independent of photometer calibration. The criterion used is the place in the band where adjacent lines of overlapping branches are of equal intensity, that is, the intersection of envelopes of the microphotometer records for the respective branches of a given band. The temperature is readily determined from graphs showing the temperature as a function of the J values at which the simultaneous requirements of equality of intensity and equality of frequency are satisfied in a given pair of branches. The method has been applied to the (0,1), (0,2), (0,3) and (0,4) bands of the Angstrom system of CO excited in the electrodeless ring discharge, both at room temperature and within a furnace at 365°C. Comparison of thermometer indications with the temperatures obtained by this method indicates (a) that the rotational energy distributions are characteristic of the temperature of the gas in the source, and (b) that the electrodeless ring discharge is a low temperature source of spectra. The error of the new method under favorable conditions may be as small as 5 percent of the absolute temperature.

INTRODUCTION

THE relative intensities of the lines in a band are determined by the proportionate numbers of molecules in the initial rotational states, and the transition probabilities for the states in question. If thermal equilibrium exists the intensity distribution can be computed from well-known formulas.[1] Even in cases where thermal equilibrium is obviously not attained, intensities may indicate a distribution of rotational energies corresponding to some effective rotational temperature. In particular, in a glow discharge where electronic bands requiring excitations of several volts are being emitted, the rotational energies may be in equilibrium with the unexcited molecules of the gas at a temperature only slightly above room temperature.

Although band intensity data have been used for estimating temperatures of both celestial and

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[1] W. Jevons, *Report on Band Spectra of Diatomic Molecules* (1932).