

ization energies are  $F_{3b} = -0.16\alpha_-e^2/d^4$  and  $F_{3a} = -(2.22\alpha_+ + 0.41\alpha_-)e^2/d^4$ .  $\alpha_+$  and  $\alpha_-$  stand for the polarizabilities of the alkali and the halogen ion. The total energy difference between the two transitions  $A$  and  $B$  comes out to be:  $\Delta = 1.032e^2/d - (2.22\alpha_+ + 0.25\alpha_-)e^2/d^4$ . If we express the energy in electron-volts,  $d$  in  $10^{-8}$  cm and the polarizabilities in  $10^{-24}$  cm<sup>3</sup>, we obtain:

$$\begin{aligned}\Delta &= 14.8/d - (31.8\alpha_+ + 3.58\alpha_-)/d^4 \\ &= \Delta_1 - \Delta_2.\end{aligned}$$

In Table III we list  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta$ , and the experimental values  $B - A$ . The latter two are not equal as they should be, but they are about of the right order of magnitude, which is all we can expect in view of the fact that the polarization energies are calculated from a rather crude model and that the exchange energies are neglected altogether.

In the case of the  $K$  edge of the  $K^+$ , for which experimental data are available too, a complication arises which makes it difficult to calculate with the above model the separate levels of the trapped states. The terms come out very nearly equal, but since the terms are diagonal

elements of the energy matrix, their difference should be large compared with nondiagonal elements. The nondiagonal elements arise from integrals containing products of series electron wave functions which are concentrated around different ions. Without knowing their values numerically, it is reasonable to assume that they are appreciable, since the overlapping of the wave functions of two series electrons from different ions is more prominent than that of closed shells, which are nearer to their respective nuclei. The overlapping of closed shells, however, is responsible for the repulsive forces between the ions, which balance the ionic attraction.

This is not an argument against the assumption that the observed maxima of absorption in the immediate neighborhood of the edge are due to transitions into trapped states, but only against the method of calculating them. Thus, the apparent failure to get a support of the "trapped states theory" in case of the  $K$  edge of  $K^+$  does not invalidate the support that we can draw for this theory from the results in case of the fine structure of the  $Cl^-$  edge in the alkali chlorides.

## A New Ultraviolet Band System of Silver Iodide

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A new ultraviolet band system of AgI has been photographed in absorption at temperatures 700–900°C. At higher temperatures the system is overlapped by strong continuous absorption, which advances gradually from shorter wave-lengths. The new system lies at 2300Å, i.e., at shorter wave-lengths than the known system, and its lower state vibrational constants agree with those given by Brice for the lower state of the longer wave-length system. The rotational structure and the very small isotope effect are not resolved. The equation for the band heads may be written

$$\begin{aligned}\nu_h &= 44,724 + 152.8(v' + \frac{1}{2}) - 1.1(v' + \frac{1}{2})^2 \\ &\quad - 205.1(v'' + \frac{1}{2}) + 0.43(v'' + \frac{1}{2})^2.\end{aligned}$$

This formula is based upon progressions from  $v' = 0$  to  $v' = 4$  and from  $v'' = 0$  to  $v'' = 11$ . An additional new band system was found at 2150Å, and the wave numbers of the band heads may be represented by the following formula:

$$\begin{aligned}\nu_h &= 45,487 + 176(v' - b + \frac{1}{2}) - 2.5(v' - b + \frac{1}{2})^2 \\ &\quad - 205(v'' - a + \frac{1}{2}) + (v'' - a + \frac{1}{2})^2;\end{aligned}$$

the values of  $a$  and  $b$  could not be determined.

### INTRODUCTION

FRANCK and Kuhn<sup>1</sup> were the first to observe bands in the spectrum of silver iodide. They

photographed bands in absorption and in resonance in the region 3100–3500Å; overlapping continuous absorption was also reported. Additional bands, diffuse in nature, at longer wave-lengths, and a weak continuum having a maxi-

<sup>1</sup> J. Franck and H. Kuhn, *Zeits. f. Physik* **43**, 164 (1927).

mum at 4000A, were mentioned by Kuhn<sup>2</sup> in a later work. However, it was Brice<sup>3</sup> who first assigned vibrational quantum numbers to the 3.8-ev system. Later he examined the system under high dispersion and succeeded in giving a more complete analysis, aided by the first measurements of the silver isotope effect.<sup>4</sup>

More recently, Mulliken<sup>5</sup> discussed the nature of predicted band systems and continua of silver chloride, bromide and iodide farther in the ultraviolet. Soon after, Jenkins and Rochester<sup>6</sup> reported the existence of a new system of silver chloride in the region 2100–2500A. In the present work, data are presented for a new band system of AgI extending from 2175–2350A. In addition, the analogous system of AgBr has been photographed; the results will be reported in the near future.

#### EXPERIMENTAL

The silver iodide obtained from Merck was introduced into the quartz absorption tube without further purification. In the early experiments silver iodide was introduced into a cylindrical vessel of transparent, fused quartz, which was then evacuated and sealed while the salt was heated somewhat above its melting point. The diameter of the tube was 2 cm and its length 20 cm. A two-unit cylindrical furnace was constructed so that each end of the tube could occupy the center of one of the units. The results were not entirely satisfactory, because at the necessary temperatures (700–900°C) the salt vapor condensed slightly on the windows and attacked them. The photographs showed that the transmitted intensity was very much reduced in the region under investigation; because, first,

the transmission of the quartz at such high temperatures is very poor for these short wavelengths and, second, the loss by scattering by condensed particles of the salt is considerable.

The apparatus was improved by keeping the windows cool. An opaque quartz tube of length 80 cm was wound with Nichrome wire save for 15 cm at each end. Windings were less numerous at the center of the furnace in order to assure a more uniform temperature distribution along the tube. Water-glass was applied to the windings and dried slowly over a flame—this kept the wire in position and in good contact with the surface. Finally the wired portion was wrapped with asbestos to a thickness of three cm. After two hundred hours at temperatures ranging from 700° to 900°C, the tube was still in very good condition. Water-cooled metal sleeves were used at each end of the quartz tube, and to these the windows were fixed with Picein. No clouding of the windows took place, even though the system was evacuated to about one mm Hg pressure to remove the absorption by heated oxygen. The light source was a hydrogen discharge tube of the conventional type, operated at 0.8 amp. and about 3000 volts. The spectra were taken with a Hilger E-3 spectrograph with a slit-width of 0.015 mm; exposures were about fifteen minutes. The plates were measured with copper lines as standards; the accuracy was approximately  $\pm 0.01$  mm corresponding to about  $\pm 2.5$   $\text{cm}^{-1}$ . Some experiments were tried on a Bausch and Lomb large Littrow spectrograph to utilize the latter's high resolving power and dispersion.<sup>7</sup> The resolution would have sufficed to permit measuring the isotope effect for making the vibrational quantum number assignment definite, but the intensity of the light source unfortunately proved insufficient.

<sup>7</sup>I wish to thank Dr. Mark Fred of the Standard Oil Company of Indiana for the use of the spectrograph, and also for his very kind cooperation.

<sup>2</sup> H. Kuhn, *Zeits. f. Physik* **63**, 456 (1930).

<sup>3</sup> B. A. Brice, *Phys. Rev.* **35**, 960 (1930).

<sup>4</sup> B. A. Brice, *Phys. Rev.* **38**, 658 (1931).

<sup>5</sup> R. S. Mulliken, *Phys. Rev.* **51**, 310 (1937).

<sup>6</sup> F. A. Jenkins and G. D. Rochester, *Phys. Rev.* **52**, 1141 (1937).

TABLE I. *Vibrational analysis of 5.52-ev system of silver iodide.*

$v'$	$v''=0$	1	2	3	4	5	6	7	8	9	10	11
0	44695	44492	44289	44087	43886	43686	43486	43285	43087	42890		
1	44845	44642	44439	44236	44037	43837	43638	43436	43238	43041	42842	
2	44993	44791	44589	44386	44187	43984			43387	43190	42991	42794
3	45139	44936	44735							43337	43138	
4	*	*								43484	43285	43086

\* Blended.

## RESULTS AND ANALYSIS

The plates show in the region below 2400A features which are now observed for the first time. When the temperature of the AgI is raised, a continuum advances from the short wave-length side. At a temperature of 775°C the region below 2260A showed seventy-five percent or more absorption; fifty percent absorption was estimated for the region 2260–2360A, and very little absorption above 2360A. Superimposed on this continuum, sharp band heads appear in the region 2175–2350A. The bands degrade to the red and form sequences. The most intense bands are near 2230A. The analysis of this system is given below. The wave numbers of its band heads are given in the conventional arrangement in Table I. The general formula for the wave numbers of the band heads of the new system is

$$\nu_k = 44,724 + 152.8(v' + \frac{1}{2}) - 1.1(v' + \frac{1}{2})^2 - 205.1(v'' + \frac{1}{2}) + 0.43(v'' + \frac{1}{2})^2. \quad (1)$$

The lower state vibrational constants are identical<sup>8</sup> with those given by Brice for the lower state of the longer wave-length system. Hence the lower state of the new system is the normal state. The  $v'=0$  level is 5.52 ev above the ground level and 1.68 ev higher than the zero vibrational level of the previously known excited state. From application of the Franck-Condon principle to the observed intensities, the equilibrium distance of the new electronic state should be larger than that of the normal state.

## ABSORPTION BANDS IN OTHER SPECTRAL REGIONS

Several additional band heads, beyond those given above, were observed. They were diffuse in nature, and accurate measurements could not be made. The results, which may be in error by several wave numbers, are given in Table II.

TABLE II. Wave numbers of band heads that are part of another electronic band system whose excitation energy is greater than 5.6 ev.

$v'$	$v''=a$	$a+1$	$a+2$	$a+3$
$b$		45270		
$b+1$	45641	45439	45239	
$b+2$		45598	45401	45210
$b+3$			45561	45363

<sup>8</sup> The fact that band heads, and not band origins, are measured may account for the difference of 1  $\text{cm}^{-1}$  in  $\omega''$ .

It appears that they are transitions to a new electronic state of higher excitation energy. The lower level should be the known ground level of AgI. With this assumption, supported by observed  $\Delta\nu$ 's, the following formula represents the observations:

$$\nu_k = 45,487 + 176(v' - b + \frac{1}{2}) - 2.5(v' - b + \frac{1}{2})^2 - 205(v'' - a + \frac{1}{2}) + (v'' - a + \frac{1}{2})^2, \quad (2)$$

where  $a$  and  $b$  are integers that could not be determined. The accuracy is approximately  $\pm 5 \text{ cm}^{-1}$ .

The possibility that iodine bands in this spectral region originating from iodine formed by the thermal decomposition of silver iodide might account for part of the observed spectrum was checked by taking photographs of iodine vapor of 0.2-mm pressure at 850°C. No absorption by  $\text{I}_2$  was found below 5000A.

On some plates the NO  $\gamma$ -bands were observed in absorption. Evidently NO was formed from the residual air in the hot quartz tube, probably under the action of the ultraviolet irradiation.

In the visible region there is absorption, with a maximum at 4000A, at the same vapor pressure<sup>9</sup> necessary for photographing the band system of Franck and Kuhn. One or more band systems are evident, covering the whole range between the 3.8-ev system and the visible absorption bands of iodine. The diffuse bands reported by Kuhn<sup>9</sup> represent only a part of the very numerous band heads appearing in this region. The bands are of nearly equal intensity and more or less evenly spaced, showing a slow convergence at shorter wave-lengths. The absence of apparent sequences or progressions cannot be explained easily.

A new thermodynamical calculation of the dissociation energy of AgI has been made recently by Beutler and Metropolis, and a value of 2.93 ev is found for the dissociation energy, higher than previously supposed. In connection with a report on this calculation, it is planned to give the analysis of the band system in the region of 4000A and a discussion of the potential energy curves of the several AgI states now known.

The writer wishes to acknowledge the encouragement and the invaluable suggestions of Professor Robert S. Mulliken and of Dr. H. G. Beutler.

<sup>9</sup> Contrary to the report of H. Kuhn, Zeits. f. Physik **63**, 469 (1930) that very high temperatures are required.