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THE ISOTOPE EFFECT IN BAND SPECTRA, III. THE  
SPECTRUM OF COPPER IODIDE AS EXCITED BY  
ACTIVE NITROGEN

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ABSTRACT

**Excitation of spectra by active nitrogen.**—Band spectra of CuF, CuCl, CuBr, and CuI have been obtained by the action of active nitrogen on the vapors of CuF<sub>2</sub>, CuCl and CuCl<sub>2</sub>, CuBr<sub>2</sub>, and CuI, using the method of Rayleigh and Fowler, as previously applied by them to CuCl. Certain additional heads are present in the red, probably due to CuO formed as a result of slight oxygen impurity in the active nitrogen, and then excited by the latter. The halide bands are unusually sharp. Probably excited N<sub>2</sub> molecules, in "impacts of the second kind," put halide molecules into the various excited electronic states necessary for the emission of visible band spectra. Many impacts, however, result in dissociation of the halide molecule, as the iodine arc line  $\lambda 2062$  and over 80 lines of the copper arc spectrum were identified. The list of copper lines is exactly the same for CuCl as for CuI. Analogous results have been obtained with PbI<sub>2</sub>, HgI<sub>2</sub>, and HgBr<sub>2</sub>. Other reactions of active nitrogen are discussed.

**Emission of electronic band spectra by polar molecules.**—It is suggested that the absence of electronic band spectra for the hydrogen, silver and alkali halides may be associated with the non-occurrence of higher valence compounds of type NaCl<sub>2</sub>, and that the emission of any one of the CuX band spectra follows the transfer of a Cu<sup>+</sup> electron in the polar Cu<sup>+</sup>X<sup>-</sup> molecule from its normal state to one of a group of low lying excited states, whose existence can be correlated with the occurrence of the compounds CuX<sub>2</sub>, such easily excited electrons being absent in ions such as Na<sup>+</sup>. The above relation may be accounted for by supposing that polar molecules cannot carry electronic energy in excess of their heat of dissociation into atoms. By analogy with the observed absence of electronic band spectra for compounds of the NaCl type, the band spectra of the alkaline earth halides should not be due to compounds MeX<sub>2</sub>, since the Me<sup>++</sup> ion contains no easily excited electron. The real emitter is probably MeX, which must contain a loosely bound valence electron like that in Me<sup>+</sup> or in Na.

**Analysis of band spectrum of CuI, and confirmation of vibrational isotope effect.**—The CuI bands, excited by active nitrogen, were photographed under moderate dispersion (see Plate I). The wave-lengths of over 260 heads between  $\lambda 5650$  and  $\lambda 3890$  were measured (Tables I-V). No other CuI bands are present between  $\lambda 1900$  and  $\lambda 7000$ . Each Cu<sup>63</sup>I band is found to be accompanied,

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wherever resolution and intensity are sufficient, by a weaker  $\text{Cu}^{63}\text{I}$  band, as expected. The  $\text{Cu}^{63}\text{I}$  bands can all be arranged in *five systems*, the vibrational isotope effect serving as an almost indispensable key to this analysis. One system lies in the green; the other four, with their bands closely intermingled, lie in the blue and violet. Equations are given representing the positions of all the  $\text{Cu}^{63}\text{I}$  heads within experimental error, in terms of the initial and final vibrational quantum numbers and their squares. From these equations, the corresponding theoretical equations for  $\text{Cu}^{65}\text{I}$  are calculated. The observed  $\text{Cu}^{65}\text{I}$  heads fall consistently within experimental error in the calculated positions. Near-equality of the coefficients (of both linear and quadratic terms) concerned with the final state of the molecule, shows that the five systems all correspond to a common final electronic state. This is almost certainly the normal state of the  $\text{CuI}$  molecule. Analogous relations probably hold for  $\text{CuCl}$  and  $\text{CuBr}$ , although the analysis is not yet completed. In all cases the vibration frequency is less and the interatomic distance greater for the excited states than for the normal state. The five excited states of the  $\text{CuI}$  molecule correspond to electronic energies equivalent to 2.44, 2.68, 2.70, 2.83, and 2.96 volts. An *energy-level diagram* for  $\text{CuI}$  is given, showing all the electronic and vibrational energy levels, and the observed transitions with their intensities. It is shown that the initial distribution of  $\text{CuI}$  molecules with respect to vibrational energy is of a thermal type and probably corresponds to the existing low temperature, thus differing markedly from the high-temperature non-thermal distribution characteristic of such compounds as  $\text{BO}$  and  $\text{CN}$  as excited by active nitrogen. *Intensity distribution in the  $\text{CuI}$  bands.* A marked tendency is noted here, as previously in the case of  $\text{BO}$ , for numerically large values of  $\Delta n$  to be associated with large values of the initial vibrational quantum number  $n'$ . This causes the maximum of intensity in band sequences (a sequence contains bands for all of which  $\Delta n$  has the same value) to shift from the first to higher members of the sequence, as one proceeds to bands at increasing distances from the system-origin. Both the above effect and a preference for positive values of  $\Delta n$  are explained in terms of Lenz's theory.

#### INTRODUCTION

THE band spectra of the chloride, bromide, and iodide of copper are highly characteristic, and that of the chloride in particular has been the object of much study.<sup>2,3,4</sup> These spectra all lie in the visible. They consist of numerous groups of bands, every group and every individual band being shaded toward the red. For the appearance of these bands, reference may be made to Eder and Valenta's excellent reproductions.<sup>3</sup> The bands are easily excited by the addition of either cuprous salts ( $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ) or cupric salts ( $\text{CuCl}_2$ ,  $\text{CuBr}_2$ ) to flames. Cupric salts easily lose their second halogen atom on heating;  $\text{CuI}_2$  is so unstable that it cannot be made even at room temperature. Hence, since the cu-

<sup>2</sup> For a summary of the literature, see Kayser and Kayser-Konen, *Handbuch der Spektroskopie*, vols. V, VII, section on Cu.

<sup>3</sup> J. M. Eder and E. Valenta, *Atlas typischer Spektren*, Vienna, 1911.

<sup>4</sup> The copper halides are also briefly discussed in H. M. Koenen's "Das Leuchten der Gasen und Dämpfe," F. Vieweg und Sohn, Braunschweig, 1913, on pp. 212, 234-5 and 275-6.

pric salts give the same spectra as the corresponding cuprous salts, the spectra have been attributed to the latter.<sup>5</sup> This is confirmed by a quantum theory analysis of the spectra (see below) which shows them to be of the type to be expected for diatomic molecules. The spectrum of copper fluoride ( $\text{CuF}_2$ ) differs from those of the other halides in that it is not readily excited, and in that it consists, so far as is known, only of a single group of bands, which, furthermore, are shaded toward the violet.

Since fairly large isotope effects were to be anticipated in these spectra,<sup>6,7,8</sup> the present study of them was undertaken. The predicted "isotope patterns" have been represented in a diagram on p. 133 of a previous article<sup>8</sup> which will be referred to as (I) in the remainder of the present discussion, and have been confirmed in the actual spectra.<sup>7,8</sup> From the atomic weight, 63.57, the two isotopes of copper which Aston has reported,<sup>9</sup>  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$ , should have an abundance ratio of about 5:2. The largest predicted separation between corresponding bands of  $\text{Cu}^{63}\text{X}$  (where X is any halogen) is for  $\text{CuI}$ , whose spectrum, furthermore, is less complicated than those of  $\text{CuBr}$  and  $\text{CuCl}$ , due to the absence of iodine isotopes. Examination of the  $\text{CuI}$  spectrum was therefore first undertaken. The results of an analysis of the green  $\text{CuI}$  bands have already been reported briefly.<sup>7</sup> The remainder of the  $\text{CuI}$  spectrum has now been analyzed, and the complete data and analysis are given below, together with preliminary and general results on  $\text{CuCl}$  and  $\text{CuBr}$ . The latter will be treated more in detail in a later paper.

#### USE OF ACTIVE NITROGEN IN EXCITATION OF COPPER HALIDE SPECTRA

In their classic work on active nitrogen, Rayleigh and Fowler showed<sup>10</sup> that the  $\text{CuCl}$  band spectrum can be excited by the introduction of  $\text{CuCl}$  vapor into the nitrogen afterglow. They reported that the  $\text{CuCl}$  bands are better visible than in the flame, the usual continuous background<sup>11</sup> in the green being absent. They also found more bands than usual at the ultraviolet end, and further noted that the copper

<sup>5</sup> R. Derichsweiler, Dissertation Bonn, 1906; *Zeits. wiss. Phot.* **4**, 401-17 (1906).

<sup>6</sup> R. S. Mulliken, *Nature*, April 5, 1924.

<sup>7</sup> R. S. Mulliken, abstract of paper given at meeting of Amer. Phys. Soc., *Phys. Rev.* **23**, 767 (1924).

<sup>8</sup> R. S. Mulliken, *Phys. Rev.* **25**, 119 (Feb., 1925): *The Isotope Effect in Band Spectra*, Part I.

<sup>9</sup> F. W. Aston, *Isotopes*, 2nd ed., 1924. Edw. Arnold & Co., London.

<sup>10</sup> R. J. Strutt, *Proc. Roy. Soc.* **85A**, 219 (1911);

R. J. Strutt and A. Fowler, *Proc. Roy. Soc.* **86A**, 105 (1911).

<sup>11</sup> This is observed in the flame spectra of all copper salts. Apparently it is not really continuous but consists (see ref. 3) of numerous closely-spaced bands (oxide bands?).

arc spectrum was developed, more lines being present than in the flame.

On account of the sharpness and clearness of the heads, and also because of interesting possibilities in regard to the mechanism of excitation, the writer has used active nitrogen as a means of exciting the spectra of all the copper halides. It was found that the bromide ( $\text{CuBr}_2$  was used) and especially the iodide, ( $\text{CuI}$ ) are less readily excited than the chloride (either  $\text{CuCl}$  or  $\text{CuCl}_2$ ), more intense heating and longer exposures being required. Also, the iodide band spectrum is largely masked by the presence of even a small amount of chloride impurity. The intensity of the copper line spectrum, relative to that of the band spectrum, appears to increase markedly in going from chloride to iodide. These differences would seem to be correlated with decreasing stability of the molecules in the order chloride-bromide-iodide. The excitation of the fluoride spectrum, by heating  $\text{CuF}_2$  in active nitrogen, was found even more difficult than that of the iodide spectrum, perhaps on account of the involatility of  $\text{CuF}_2$ ; some weak exposures were, however, obtained.

*Oxide bands.* With all three halides, a set of bands, of variable intensity, occurs in the red. These proved, by approximate determination of their wave-lengths and comparison with Eder and Valenta's excellent reproductions,<sup>12</sup> to be the red bands which are ascribed by Eder and Valenta to copper oxide ( $\text{CuO}$ ), and which occur in the flame spectra of all copper salts. The heads of the bands appear for the most part in pairs, all the heads being shaded toward the red. According to the literature, the members of a pair are ordinarily about equally intense, but in the present experiments, the shorter wave-length component was relatively weak. The following list covers the observed heads, the intensities being given in parentheses, for an unusually intense exposure. The wave-lengths were not carefully measured, but Hertenstein's values<sup>13</sup> are given approximately, except for three apparently new heads at the red end for which the (only roughly approximately) wave-lengths are italicized:  $\lambda$ 6046 (1), 6060 (7); 6148 (2), 6163 (8); 6283 (00?), 6296 (2); 6381 (0), 6403 (1), *6435* (3); *6490* (1), *6530* (1), 6547 (2). Only the stronger heads (int. 2 or

<sup>12</sup> Eder and Valenta.<sup>3</sup> Plates V, 2-3, XXI, 9, and XXV, 8, show these bands especially well. In plate XXI, 9, the stronger heads are shown resolved into what is probably a succession of heads, so that each "head" as used above probably means the first head of a compact group. Kayser and Konen<sup>2</sup> consider it rather doubtful whether these and other bands toward shorter wave-lengths are due to the oxide or the metal. Some of the copper bands of large spacing, as well as other supposed metal bands, have recently been shown (see ref. 6) to be due to a hydride. The red bands are not of this type. It is of course still possible that they are due to  $\text{Cu}_2$ .

<sup>13</sup> H. Hertenstein, *Zeits. wiss. Phot.* **11**, 69 and 119 (1912).

more) were definitely observed to be shaded toward the red. It may be noted that only the heads from  $\lambda 6046$  to  $6296$  are found in the Bunsen flame, according to Eder and Valenta, while the oxy-gas flame is needed for the following pair. The occurrence of the bands here is presumably due to the excitation of oxide molecules by active nitrogen. A detailed investigation did not seem worth while, but there was evidence that the bands are favored by a small leakage of air into the halide vapor, or the presence of a little oxygen in the nitrogen used. A dark brown or black deposit, presumably copper oxide, formed in small amounts on the walls of the afterglow tube, was formed more rapidly when air was admitted. This product, separated from copper halide by dissolving the latter in sodium thiosulphate solution, was at first suspected of being a nitride. On heating it with NaOH solution, a strong odor of ammonia was in fact obtained in one case when CuBr had been used (in this case the NaOH was added directly to the thiosulphate solution containing the solid in suspension). Since, however, later tests with Nessler's reagent failed to give any indication of ammonia with the product obtained from CuI, and only a slight test with the CuCl product, the formation of nitride in appreciable amounts must be considered very doubtful.—There is no evidence in the present work of a nitride band spectrum.

#### EXPERIMENTAL METHODS AND WAVE-LENGTH DATA

In producing the active nitrogen, the method used was essentially that of Lord Rayleigh.<sup>14</sup> Commercial nitrogen (99.7 per cent pure according to the manufacturers) contained in a cylinder under pressure was passed through successive tubes containing (a) fragments of yellow phosphorus (b) calcium chloride, (c) soda-lime, (d) phosphorus pentoxide.

The product was usually very nearly free from oxygen—the  $\beta$  and  $\gamma$  bands of active nitrogen, which are due to the presence of oxygen, being very weak—and sometimes contained excess phosphorus vapor. Any considerable amount either of oxygen or of phosphorus vapor caused a marked decrease in the intensity of the copper halide bands. In experiments with CuCl where excess phosphorus vapor was present, it was found that the CuCl spectrum was restored to its original brilliancy by the admission of a small amount of air, sufficient to destroy the phosphorus. The effect was the same whether this was added before or after the activation of the nitrogen, and the amount required had no visible effect on the color or intensity of the afterglow itself.<sup>15</sup>

<sup>14</sup> R. J. Strutt, Proc. Roy. Soc. **85A**, 219 (1911).

<sup>15</sup> The effect of adding oxygen here was evidently of an entirely different nature from that in the case of BO (R. S. Mulliken, Nature, Sept. 6, 1924), where no excess of phosphorus was present.

## DESCRIPTION OF PLATE I

Plate I shows most of the CuI bands; *top*, A bands; *middle*, B, C, most of D, and part of E bands; *bottom*, one D band and part of E bands (there are probably a few more, not shown, toward the ultraviolet). Each Cu<sup>63</sup>I head is marked with a vertical line. Each horizontal line serves to connect the members of a band-sequence, i.e. a set of bands having a common value of  $(n''-n')$ ,  $n''$  and  $n'$  being the final and initial vibrational quantum numbers. For each system, the first head  $(n', n'') = (0, 0)$  of the (0) sequence is marked by a *very* heavy vertical line, accompanied by the letter (A, B, etc.) which has been assigned to the system. With this as an origin, the numbering of the other sequences and of the individual bands can be found very readily from the reproduction. Thus, in the A system, the (0) sequence, from left to right, contains the bands (0,0), (1,1), (2,2), (3,3), . . . The next sequence (+1) on the right, contains the bands (0,1), (1,2), (2,3), (3,4), (4,5), . . . On the left of the origin is the (-1) sequence, with bands (1,0), (2,1), (3,2), (4,3), (5,4), . . . ; with the (5,4) head, this sequence slightly overlaps the (0) sequence. It will be noted that on each side of the origin the spacing of the first heads of successive sequences is approximately constant, but that it differs markedly for the positive and negative sequences. This is because these first heads are (0,0), (1,0), (2,0), (3,0), . . . for the negative, and (0,1), (0,2), (0,3), . . . for the positive sequences. For the former the spacing is determined by the *initial*, for the latter by the *final*, vibration frequency of the molecule. To avoid confusion, alternate sequences have been marked in the A bands by verticals of different height; while in the B, C, D, and E bands, which are badly mixed together in the middle of the spectrum, a vertical of characteristic height (diminishing in the order named) is used for each.

The A bands in particular show a typical intensity distribution. As can be seen in the reproduction, the sequences near the origin are the most intense, with some preference for the positive sequences. In the low-numbered sequences, the first head is the most intense, but the intensity maximum shifts to the second head with the sequences  $\pm 3$ , and to higher-numbered heads for the higher sequences.

For each Cu<sup>63</sup>I head, there is a corresponding weaker Cu<sup>65</sup>I head *nearer the origin* in each case. These begin to be resolved at about the sequences  $\pm 2$ . In the reproduction, resolution is apparent in the A system at +3, in the other systems (except B, which is too faint) at +2. In the negative sequences, the Cu<sup>65</sup>I heads are not visible, except rather vaguely in the A sequences -3 and -4. This is due partly to low intensity, partly to concealment by the shading of corresponding Cu<sup>63</sup>I heads. Examination of the manner in which, in the positive sequences, the separation between the heads of the two isotopes converges toward zero as the origin is approached, will show the value of the isotope effect as a means of locating the latter. (Casual inspection of the reproduction would probably lead to a false assignment, due to the different intensities of the heads of the two isotopes; the (+1) sequence would probably be called (0). Careful inspection of the original negative, however, and especially measurement gives the correct assignment without difficulty.)

BANDS OF COPPER IODIDE



Plate I. Spectrograms showing most of the CuI bands.

The discharge tube for activating the nitrogen, and the attached afterglow tube, were of Pyrex glass of about 8 mm internal diameter. The arrangement is shown in Fig. 1. The discharge was maintained between two tungsten electrodes which were about 10 cm apart. A type E Clapp-Eastham transformer was used at maximum amperage on a 110 volt circuit, with a spark-gap and two large Leyden jars in parallel in the secondary circuit. The activated nitrogen was pumped rapidly out, through a black-painted light trap *T*, into the afterglow tube. The latter was attached at right angles to the discharge tube. The copper salt was contained in a small bulb *B* connected to the afterglow tube at a point just below the point of entrance of the active nitrogen. The bulb was heated by a Bunsen flame just short of its softening point. The quartz

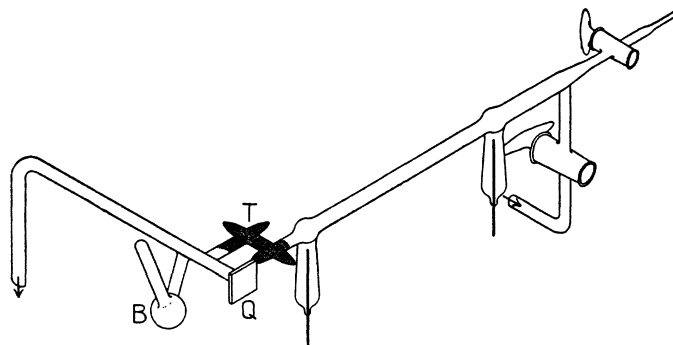


Fig. 1. Arrangement of discharge and afterglow tube for exciting spectra by means of active nitrogen.

window *Q*, fastened with DeKhotinsky cement, was kept cool by means of a ring of wet filter paper on the adjacent section of the afterglow tube. The discharge tube terminal nearer the afterglow tube was earthed, to prevent stray discharge through the latter. In early experiments, where this precaution was not taken, nitrogen lines were present in the spectrum; they were absent from the later photographs, although nothing else was changed. A nitrogen flow rate of 20-60 liters (at 1 atmosphere pressure) per hour was used, with a pressure of about 15-40 mm in the afterglow tube.

The spectra were photographed with a Hilger glass constant-deviation prism spectrograph. The dispersion ranged from about 12 Å/mm at  $\lambda 4000$  to 36 Å/mm at  $\lambda 5000$  and 72 Å/mm at  $\lambda 6000$ . Panchromatic, special green-sensitive, and contrast plates were used for best results with the red, green, and blue to violet regions, respectively. The ultra-violet was examined with quartz spectrographs.

As wave-length standards for the bands, the interspersed Cu lines were used, supplemented by helium lines (plus  $H\beta$ ,  $H\gamma$ , and  $H\alpha$ ) from a super-



posed comparison spectrum, and in the yellow-green, where Cu lines were scarce, by certain N<sub>2</sub> band-heads of the first positive group ( $\alpha$  bands of the afterglow); the latter are very sharp and appear to have been measured accurately to 0.01A. In one photograph N lines resulting from stray discharge (see above) were also available.

In the case of CuI, the exposure used for measurement was one of about three hours duration on a special green-sensitive plate. Enlargements from this are shown in Plate I. The type of plate used is fine-grained, and so, with good focus and a narrow slit, permitted unusually good resolution for the size of the instrument. Practically every distinct head on the plate, including very weak ones, was carefully measured. The results are given in Tables I-V. It can be stated definitely that there are no additional bands of appreciable intensity, at least in the region  $\lambda$ 1900-7000. The precision of the measurements can be gauged by the magnitude of the values in the Obs.-Calc. (O-C) columns. A slight constant error is

TABLE I

*A bands*

Note for Tables I-V: The vibrational quantum numbers are given under  $n'$  and  $n''$ . The "calculated" wave-numbers used for computing the values under "O-C" (observed minus calculated) for Cu<sup>63</sup>I and in obtaining the calculated isotopic displacements, were obtained from the equations of Table 6. Isotopic displacements, i.e.  $\nu(\text{Cu}^{65}\text{I}) - \nu(\text{Cu}^{63}\text{I})$ , are given in wave-number units. Wave-numbers in brackets are calculated values, inserted where measurements were not obtained. Nitrogen lines (due to stray discharge, see above), of which a small number were present, and which in some cases (marked "also N line") were superposed on CuI heads, could be picked out by the fact that they extended beyond the CuI heads at the edges of the exposure.

$n'$	$n''$	Cu <sup>63</sup> I heads			Cu <sup>65</sup> I heads			Isotopic displacement	
		Int.	$\lambda$ (I.A.)	Wave-no. O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
8	3	0	4886.0	20461 -10	0-*	4887.6	20454	-7	-6.7
4	0	0	72.77	516.5 -2	0*	74.69	508.4	-8.1	-8.0
5	1	0+	89.57	446.0 0	0+*	91.15	439.4	-6.6	-7.1
6	2	0	4917.93	369.5 -1	0*	4909.40	363.4	-6.1	-6.2
7	3	00	28.4	285 -7	00*	29.6	280	-5	-5.2
3	0	1	19.09	323.3 1	1*	20.86	316.0	-7.3	-6.1
4	1	1	35.59	255.4 1	1-*	36.73	250.7	-4.7	-5.4
5	2	0	53.16	183.5 0	0*	54.19	179.3	-4.2	-4.5
6	3	00		[ 109.3]					
7	4	00		[ 031.9]					
2	0	3	68.33	121.9 0		69.24	118.2	-3.7	-4.2
3	1	2	83.88	059.1 0		84.85	055.2	-3.9	-3.5
4	2	0		[1992.2]					
5	3	00		[ 920.4]					

\* The high apparent intensities of the Cu<sup>65</sup>I heads in this region are due to their superposition on the shading from corresponding Cu<sup>63</sup>I heads.

TABLE I—continued

$n'$	$n''$	Cu <sup>63</sup> I heads			Cu <sup>65</sup> I heads			Isotopic displacement	
		Int.	$\lambda$ (I.A.)	Wave-no. O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
1	0	5	5019.74	915.8 -1				-2.1	
2	1	1	34.61	857.0 -1				-1.6	
3	2	000		[ 796.3]				-0.9	
4	3	0	66.65	731.4 0				-0.2	
5	4	0+	84.52	662.1 -1				0.6	
6	5	00		[ 591.5]					
0	0	7	72.83	707.4 0				0.0	
1	1	0+	87.16	651.9 -1				0.5	
2	2	1	5101.92	595.0 -1				1.0	
3	3	1	17.31	536.1 1				1.6	
4	4	000		[ 471.5]					
0	1	5	41.12	445.6 2					
1	2	1	55.84	390.1 -1					
2	3	00-	70.75	334.2 -1	000		[19338.7]		
3	4	0	86.80	274.4 -1	00	5185.95	277.5	3.1	3.6
4	5	0	5202.74	215.3 2	00	5201.18	221.1	5.8	4.9
0	2	5	12.18	180.5 -1	2	10.71	185.9	5.4	5.2
1	3	3	26.08	129.5 0	1	24.28	136.1	6.6	5.7
2	4	1	41.03	074.9 0	0	39.25	081.4	6.5	6.1
0	3	2	83.80	18920.5 0	0	81.80	18927.7	7.2	7.8
1	4	4	97.55	871.4 1	1	95.17	879.9	8.5	8.2
2	5	3	5312.42	818.6 2	1	5310.05	827.0	8.4	8.7
3	6	1	28.53	761.7 1	0	26.09	770.3	8.6	9.2
4	7	00	45.8	701 -1	000	43.8	708	7	9.8
5	8	0	64.09	637.3 -1	0	61.3	647	10	10.5
0	4	1	57.42	660.5 0	0	54.27	671.5	11.0	10.3
1	5	3	71.47	611.7 0	1	68.16	623.2	11.5	10.7
2	6	4	86.50	559.8 0	2	83.22	571.1	11.3	11.1
3	7	3†	5402.18	506.1 1	1	98.74	517.7	11.6	11.6
4	8	1-	18.94	448.7 1	0-	5415.71	459.7	11.0	12.2
0	5	0	33.48	399.3 -3	00	28.03	417.8	18.5	12.9
1	6	0+	46.60	355.0 0	1†	42.41	369.1	(14.1)	13.2
2	7	1	61.30	305.6 1	0	57.45	318.5	12.9	13.6
3	8	2	77.09	252.8 1	1	73.04	266.3	13.5	14.1
4	9	1	94.07	196.4 2	0	89.88	210.3	13.9	14.6
5	10	0	5512.79	134.6 -1	00	5507.72	151.3	16.7	15.3
0	6			[ 145.4]					15.3
1	7	00	24.34	096.7 -3	000	19.1	114	17	15.6
2	8	0	38.88	049.2 -2	00	34.07	064.9	15.7	16.0
3	9	1-	54.02	000.0 1	0	48.16	019.0	19.0	16.5
4	10	0+	71.04	17945.0 1	0-	65.21	17963.8	18.8	17.0
5	11	0	88.76	888.1 3	00	83.29	905.6	17.5	17.6
6	12	00	5608.9	824 0	00	5603.8	840	16	18.3
2	9	000	17.3	797 -1					18.4
3	10	00	32.5	749 1	000	26.8	767	18	18.9
4	11	00	49.7	695 1	000	43.1	716	21	19.4

† Also N<sub>2</sub> head.

Note: Average value of "observed" minus "calculated" isotopic displacement, excluding from the average only (0,5), (1,6), and bands where the Cu<sup>65</sup>I head has an intensity less than 00, is +0.05.

TABLE II

*B bands*

Note: because of the low intensity or absence of bands for which an appreciable separation of the heads of the two isotopes would be expected, no measurements could be made on Cu<sup>65</sup>I heads. Indications of the (0,2) head of Cu<sup>65</sup>I were seen, however.

<i>n' n''</i>	Cu <sup>63</sup> I heads				Remarks
	Int.	$\lambda$ (I.A.)	Wave-no.	O-C	
2 0	0-	4498.26	22224.6	0	Also 1, 8 E (Cu <sup>65</sup> I)
3 1	00	4504.79	192.4	0	
4 2	00	11.19	160.9	2	
1 0	1-	46.77	21987.5	-1	
2 1	0	52.63	959.2	-1	
3 2	00	58.11	932.8	3	
4 3			[ 897.9]		
0 0	1d	96.95	747.5	-1	Also (weak) 3,3C
1 1	1	4601.58	725.6	2	Also (strong) N line
2 2	1	07.07	699.7	2	Also (strong) N line
3 3	00	13.09	671.4	2	
4 4	00	19.95	639.2	0	
5 5	00	26.60	608.1	0	
6 6			[ 574.3]		
0 1	0+	4653.50	21483.2	-1	Also 4, 5C? A group of heads (see footnote) present here may include both B and C heads; but the data do not agree well with either.
1 2	0-	58.62	459.6	-2	
2 3			[ 437.1]		
3 4			[ 411.0]		
4 5			[ 383.1]		
5 6			[ 353.4]		
0 2	0-	4711.34	219.5	-2	Also 4,6 C?
1 3	00	15.00	203.0	2	
2 4	00	19.85	181.2	3	Fused with 5,7 C? Possibly present but confused by C heads.
3 5	00d	23.69	164.0	9	
4 6			[ 128.7]		
5 7			[ 101.0]		

Note: wave-numbers of unidentified heads, with intensities: 21342.1(00); 21357.5(00-); 21370.3(00); 21386.5(00); 21402.9(0-); 21417.7(00); 21431.2(0-); 21445.2(00); 21473.7(0); 21548.2(00); 21581.1(00?); 21657.3(00); 21691.1(00); 21710.8(00); 21739.0(00?); 21823.0(00); 21905.7(00); 22178.0(00); 22192.4(00); 22418.4(00+); 22431.9(00); 22771.0(00); 22802.4(00); 22833.3(00); 22866.8(00).

TABLE III  
C bands

$n'$	$n''$	Cu <sup>63</sup> I heads			Cu <sup>65</sup> I heads			Isotopic displacement	
		Int.	$\lambda$ (I.A.)	Wave-no. O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
3	0	weak or absent, [22534.9]							
4	1	masked by CuCl [ 497.7]							
2	0	00	4482.03	305.1 <sup>1</sup>	-3				
3	1	00?	89.81	266.4	-5				
4	2	00-	96.88	231.4	-4				
5	3	00	4502.41	204.1	4				
6	4			[ 165.3] <sup>2</sup>					
1	0	2-	27.92	079.0	-1				
2	1	0-	35.11	044.0	-1				
3	2	00	41.91	011.0	1				
0	0	2-	75.15	21851.1	0				
1	1			[ 816.9]					
2	2	masked by 5,13 E [ 782.8]							
3	3	masked by 0,0 B [ 749.2]							
4	4	00	4603.31	717.4	1				
5	5	00	10.64	682.9	0				
0	1	3?	30.63	589.3	1				
1	2	0	38.03	554.9	0				
2	3	..	...	[ 522.2]					
3	4	masked by Cu [ 489.9]							
4	5	0-	58.62	459.6 <sup>3</sup>	2				
5	6			[ 426.4] <sup>4</sup>					
6	7			[ 395.3] <sup>4</sup>					
7	8			[ 364.6] <sup>4</sup>					
8	9			[ 334.3] <sup>4</sup>					
0	2	1+	87.80	326.0	0	0	4686.84	21330.4	4.4 5.4
1	3	1-	93.97	295.3	1	0-	93.35	300.8	5.5 5.7
2	4	0-	4701.72	262.9	0	00	4700.21	269.7	6.8 6.0
3	5	00	08.72	231.3	-1				
4	6	00	14.99	203.0 <sup>5</sup>	2				
5	7	00d	23.69	164.0 <sup>6</sup>	-7				
6	8	00	29.54	137.8 <sup>7</sup>	-3				
7	9	00	35.59	110.8 <sup>7</sup>	-1				
0	3	00	45.96	064.7	-1	00	43.59	075.2	10.5 8.0
1	4	0+	52.64	035.1	0	00	50.90	042.8	7.7 8.3
2	5	00+	59.35	005.4	0	00	57.47	013.7	8.3 8.6
3	6	00-	66.14	20975.5	0	00-	64.37	20983.3	7.8 8.8
4	7	00	72.81	946.2 <sup>8</sup>	0				
5	8			[ 917.0] <sup>9</sup>					
6	9			[ 888.5]					
0	4	00?	...	[ 806.4]					
1	5	00?	...	[ 777.1]					
2	6	00?	...	[ 748.3]					

<sup>1</sup> Also 6,12 (Cu<sup>65</sup>I).<sup>2</sup> Confused by E and B heads.<sup>3</sup> Also 1,2 B.<sup>4</sup> See remark in Table II on heads in this region.<sup>5</sup> Also 1,3 B.<sup>6</sup> Fused with 3,5 B?<sup>7</sup> Confused by B heads, see Table II.<sup>8</sup> Also 0,3 B.<sup>9</sup> Confused by B.

TABLE IV  
D bands

$n'$	$n''$	Cu <sup>63</sup> I heads				Cu <sup>65</sup> I heads			Isotopic displacement	
		Int.	$\lambda$ (I.A.)	Wave-no.	O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
2	0	?0-	4281.97	23347.2 <sup>1</sup>	..					
1	0	1	4320.01	141.6	0					
0	0	2+	59.95	22929.6	0					
1	1	1+	69.93	877.3 <sup>2</sup>	-1					
0	1	3	4410.76	666.0	0					
0	2	2	62.22	404.1	0	0+	4461.08	22409.8	5.7	5.4
1	3	1	71.64	356.9 <sup>3</sup>	2					
0	3	1	4514.76	143.4 <sup>4</sup>	0	0	4513.31	150.5	7.1	8.0
1	4	0	24.69	094.8	0	0+	22.46 <sup>5</sup>	105.7	10.9	8.4
0	4	0-d	68.50	21882.9	0	0-	66.31	21893.4	10.5	10.6
1	5	0d	78.15	836.8 <sup>6</sup>	0		masked by 0,0 C			
1	6	00	4632.39	581.1	2					

<sup>1</sup> Doubtful, in shading of 3,5E.<sup>2</sup> Also 2,6 E.<sup>3</sup> Also (weak) 3,9 E (Cu<sup>65</sup>I).<sup>4</sup> Also (weak) 1,8 E.<sup>5</sup> Also 3,10 E (Cu<sup>65</sup>I).<sup>6</sup> Also 3,11 E.TABLE V  
E bands<sup>1</sup>

$n'$	$n''$	Cu <sup>63</sup> I heads				Cu <sup>65</sup> I heads			Isotopic displacement <sup>2</sup>	
		Int.	$\lambda$ (I.A.)	Wave-no.	O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
3	0	0	4054.17	24659.0	0					
4	1	..	....	[ 617.4]	..					
2	0	1	91.32	435.1	0					
3	1	0	....	[ 395.8]						
4	2	0	4105.02	353.6	-2					
5	3	0	12.34	310.2	-5					
6	4	00	18.51	273.8	0					

<sup>1</sup> Besides the heads recorded in the table, some additional weak heads, mostly further toward the ultraviolet, were found in photographs with the quartz spectrograph. These are shaded toward the red, like the other CuI bands. Several attempts were made to obtain these bands in sufficient intensity for good measurements, but this finally appeared to be not worth while. The data below were obtained with a weak exposure and wide slit. The presence of CN and CuCl bands as impurities also increased the difficulties; NO and I<sub>2</sub> bands were not present in this region. They suffice, however, in spite of poor agreement with calculated values, to establish without much doubt that the observed bands are a (not unexpected) continuation of the E bands, and not an independent system. The intensities were for the most part too low for identification of Cu<sup>65</sup>I heads. The measured values are (with calculated values in parentheses): 24526, (int. 00) (6,3 E = 24533); 24656, (0) (3,0 E = 24659); 24875, (00) (4,0 E = 24881); 24983, (00); 25045, (00) (6,1 E = 25055); 25079, (00) (5,0 E, Cu<sup>65</sup>I, = 25089); 25090, (00) (5,0 E = 25100); 25235, (00), superposed on CuCl head (8,2 E = 25223); 25265, CuCl head (7,1 E = 25271); 25311, (00d) (25318 = 6,0 E); 25378, (000d); 25493, (00d) (8,1 E = 25485); 25533, (000d) (7,0 E = 25534); 25647, (000) (9,1 E = 25697); and perhaps a few additional weaker heads.

<sup>2</sup> Average value of "observed" minus "calculated" isotopic displacement, excluding heads marked \* or ?, or of intensity less than 0, is -0.4.

TABLE V—continued

$n'$	$n''$	Cu <sup>63</sup> I heads			Cu <sup>65</sup> I heads			Isotopic displacement		
		Int.	$\lambda$ (I.A.)	Wave-no. O-C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.	
1	0	1-	29.38	209.9	0	*0?	4130.32	24204.4 <sup>3</sup>	-5.5	-2.3
2	1	0	35.82	172.2	0	*0-?	36.49	168.3 <sup>3</sup>	-3.9	-2.0
3	2	0	42.22	134.9	1					
0	0	0	68.52	23982.6	0					
1	1	2	74.60	947.6	1					
2	2	1-	80.85	910.9	0					
3	3	00	87.55	873.6	0					
4	4	0+	94.12	836.2	0					
5	5	00	4200.98	797.3	-1					
0	1	2	14.64	720.2	1	0?	.....	.....	.....	2.7
1	2	0	21.03	684.2	-1					
2	3	2-	27.00	650.8	1	0-	4226.39	23654.2	3.4	3.5
3	4	0	33.75	613.1	-1					
4	5	000	.....	[ 578.3]						
5	6	00	47.01	539.4	-2					
6	7	00	53.28	504.7	0					
0	2	3	61.74	458.1	0	1	60.72	463.6	5.5	5.4
1	3	0-	68.14	422.8	-2	...	..... [ 428.5]	.....	.....	5.7
2	4	00	74.11	390.1	-1	00	72.83	397.1	7.0	6.0
3	5	1-	80.06	357.5	1	0-	79.07	363.4	5.9	6.4
4	6	1-	86.50	322.5	1	00	..... [ 329.3]	.....	.....	6.8
5	7	000	.....	[ 286.5]						
0	3	2+	4309.62	197.4	0	1-	4308.17	205.2	7.8	8.0
1	4	1	15.42	166.2	1	0	14.06	173.5	7.3	8.3
2	5	.....	masked	[ 133.2]		*	masked	[ 141.8] <sup>4</sup>	.....	8.6
3	6	000	.....	[ 100.3]				[ 109.2]	.....	8.9
4	7	0*	masked	[ 066.8] <sup>5</sup>		00	32.30	076.0	[9.2]	9.3
5	8	0-	40.45	032.6	0	00	39.02	040.2	7.6	9.6
6	9	00	46.80	22999.0	1					
0	4	1*	58.34	938.1 <sup>6</sup>	0	0*	56.19	22949.4 <sup>6</sup>	(11.3)	10.7
1	5	2-	64.05	908.1	0	0+	62.12	918.2	10.1	10.9
2	6	1+*	69.93	877.3 <sup>7</sup>	1	0-	68.00	887.4	10.1	11.2
3	7	0-	76.11	844.9	0	00	74.11	855.4	10.5	11.4
4	8	000	82.27	812.8	0	000	79.95	824.9	12.1	11.7
5	9	00-	88.55	780.2	0	000	86.60	790.3	10.1	12.0
6	10	000	94.86	747.5	0	000	92.77	758.3	10.8	12.4
7	11	000-	.....	[ 713.2]						
0	5	0+	4408.07	679.3	-1	0-	4405.53	692.4	13.1	13.2
1	6	1-	13.75	650.1	-1	*	masked	[ 663.6] <sup>8</sup>	.....	13.5
2	7	1*	19.08	622.8 <sup>9</sup>	1	0+	16.62	635.4	12.6	13.7
3	8	1-	25.07	592.2	1	0-	22.50	605.3	13.1	14.0
4	9	0*	31.25	560.7 <sup>10</sup>	0	00	.....	[ 575.0]	.....	14.3

<sup>3</sup> Intensity doubtful.<sup>4</sup> Masked by 1,0 D.<sup>5</sup> Masked by CuCl.<sup>6</sup> Also CuCl?<sup>7</sup> Also 1,1 D.<sup>8</sup> Masked by 0,1 D.<sup>9</sup> Also 1,2 D.<sup>10</sup> Also N  $\lambda$ 4431.

TABLE V—continued

$n' n''$	Cu <sup>63</sup> I heads			Cu <sup>65</sup> I heads			Isotopic displacement	
	Int.	$\lambda$ (I.A.)	Wave-no. O—C	Int.	$\lambda$ (I.A.)	Wave-no.	Obs.	Calc.
0 6	0	58.40	423.3 -1					
1 7	1	63.60	397.2 1					
2 8	1+	69.24	368.9 1	1d	65.93	385.5	16.6	16.2
3 9	1+	75.05	339.9 1	1*+	71.64	356.9 <sup>11</sup>	17.0	16.4
4 10	1-	masked [	309.6] <sup>12</sup>	0-d	78.01	325.1	.....	16.7
5 11	0-d	86.89	280.9 1	0-	84.42	293.2	12.3	16.9
6 12	00d	93.69	247.2 -2	00	89.81	266.4	19.2	17.2
0 7	.....	masked [	168.9] <sup>12</sup>	00	4506.19	185.5	.....	18.4
1 8	1*+	4514.76 <sup>13</sup>	143.4 1	00*	11.19	160.9 <sup>13</sup>	[17.5]	18.5
2 9	0+	20.62	114.7 -1	0+	16.94	132.7	18.0	18.7
3 10	0+	26.28	087.0 -1	0*+	22.46	105.7 <sup>14</sup>	18.7	18.9
4 11	00	31.88	059.7 0	... masked <sup>15</sup> [	078.6]			19.1
5 12	0	37.65	031.7 1	0-	33.36	052.5	20.8	19.3
6 13	0d	43.71	002.3 0	00	39.07	024.8	22.5	19.5
7 14	00-	49.73	21973.2 1					
8 15	00	55.93	943.3 2					
2 10	00d	72.80	862.3 -2					21.2
3 11	0d*	78.15	836.8 <sup>16</sup> -1	masked by 2,10 of Cu <sup>63</sup> I				21.3
4 12	0d	83.46	811.5 0	masked by 3,11 of Cu <sup>63</sup> I				21.5
5 13	0d*	88.95	785.4 <sup>17</sup> 1	masked by 4,12 of Cu <sup>63</sup> I				21.7
6 14	00d	94.69	758.2 2					21.9
7 15	00	4600.23	732.0 4					
3 12	*	masked [	589.3] <sup>18</sup> -1					
4 13	00	35.80	565.2 1					
5 14	00	41.50	538.7 0					
6 15	0-d	49.24	508.9 -3					

<sup>11</sup> Also 1, 3 D.<sup>12</sup> Masked by Cu.<sup>13</sup> For 4514, also (strong) 0,3 D; for 4511, also 4,2 B.<sup>14</sup> Also (strong) 1,4 D.<sup>15</sup> Masked by 1,0 C.<sup>16</sup> Also 1,5 D.<sup>17</sup> Also 2,2 C.<sup>18</sup> Masked by 0,1 C.

likely, due to the uncertainty as to the proper mode of setting on heads which are shaded off toward one side. The following measured values for a few of the strongest CuCl heads, present as impurities among the CuI heads, may be compared with presumably much more accurate values as determined by Kien<sup>16</sup> under high dispersion:

Present results: 4333.37, 4353.93, 4412.16;

Kien, 4333.254, 4353.892; 4412.14.

Detailed data on the CuBr and CuCl bands will be reserved for a later paper.

#### ANALYSIS OF CUI BANDS

As will be seen from the tables, all the CuI bands, with a few very weak and rather doubtful exceptions, can be arranged in five band-

<sup>16</sup> P. Kien, Diss. Bonn. 1908; Zeits. wiss. Phot. 6, 337 (1908).

systems, i.e., five complex groups of bands, each associated with a particular electronic transition in the CuI molecule, accompanied by a variety of vibrational transitions indicated by the values of the initial and final vibrational quantum numbers  $n'$  and  $n''$ . For simplicity, and in the absence of direct evidence from the present analysis, integral vibrational quantum numbers are here used in accordance with the usual practice, although the isotope effect in the BO spectrum<sup>17</sup> indicates that half-integral values may be needed. The assignment of vibrational quantum numbers is such as to satisfy the criteria used by Heurlinger and Kratzer, as well as the isotope effect criterion (I, p. 136).<sup>8</sup> The isotope effect, as previously emphasized,<sup>7,8</sup> was invaluable in locating the origins of the band-systems, giving, in fact, the first clue to the analysis of the very complex spectrum. In examining the arrangements of the bands in the tables, comparison with the reproduced spectrum (Plate I, and accompanying explanation) will be useful.

In Table VI are given, for each CuI system, equations in terms of the parameters  $n'$  and  $n''$  capable of representing within experimental error the positions of all the measured heads. The possibility that cubic

TABLE VI

*Equations representing CuI heads*

Note: the equations, except those for Cu<sup>63</sup>I, were obtained by plotting the appropriate first differences; the Cu<sup>63</sup>I coefficients were calculated according to theory from those of the corresponding Cu<sup>65</sup>I equations.

*A bands*

$$\begin{aligned} \text{Cu}^{63}\text{I}: \nu &= 19,707.65 + 211.91n' - 2.283n'^2 - 264.63n'' + 0.713n''^2 \\ [\text{Cu}^{65}\text{I}: \nu &= 19,707.7 + 209.72n' - 2.236n'^2 - 261.89n'' + 0.698n''^2] \end{aligned}$$

*B bands*

$$\text{Cu}^{63}\text{I}: \nu = 21,748.3 + 241.8n' - 1.88n'^2 - 265.4n'' + 1.0n''^2$$

*C bands*

$$\begin{aligned} \text{Cu}^{63}\text{I}: \nu &= 21,851.41 + 229.17n' - 0.447n'^2 - 263.86n'' + 0.653n''^2 \\ [\text{Cu}^{65}\text{I}: \nu &= 21,851.4 + 226.80n' - 0.438n'^2 - 261.14n'' + 0.640n''^2] \end{aligned}$$

*D bands*

$$\begin{aligned} \text{Cu}^{63}\text{I}: \nu &= 22,929.66 + \frac{F(n')}{0.99} - 264.2n'' + 0.64n''^2 \\ [\text{Cu}^{65}\text{I}: \nu &= 22,929.7 + 0.99F(n') - 261.5n'' + 0.63n''^2] \end{aligned}$$

Note:  $F(n') = 212.1$  for  $n' = 1$ .

*E bands*

$$\begin{aligned} \text{Cu}^{63}\text{I}: \nu &= 23,982.71 + 228.28n' - 0.954n'^2 - 263.81n'' + 0.671n''^2 \\ [\text{Cu}^{65}\text{I}: \nu &= 23,982.7 + 225.92n' - 0.934n'^2 - 261.09n'' + 0.657n''^2] \end{aligned}$$

terms in  $n'$  (and  $n''$ ) should be used has been disregarded, since the data are not precise enough to yield significant values of the coefficients of such terms. The coefficients, and especially the constants, of Table VI are, of course, somewhat influenced (cf I, pp. 131-2) by the fact that the

<sup>17</sup> R. S. Mulliken, Phys. Rev. **25**, 259 (March, 1925).



data refer to heads, instead of to origins (I, p. 123) or null-lines. This fact does not, however, obscure certain important major relations among the various bands. In fact, the present type of analysis, in which the arrangement of bands in systems is determined without regard to band-structure, seems to the writer a desirable preliminary, in complex cases like those of the copper halides, to a more detailed analysis of individual bands under higher dispersion.<sup>18</sup>

Considering for the present only the Cu<sup>63</sup>I heads, one of the most striking facts revealed in Table VI is the near-identity of all coefficients of  $n''$  and  $n''^2$  for all five systems.<sup>19</sup> The agreement is so close as to make it extremely probable that the final electronic state (and associated vibrational states) are the same for all five systems. The differences in the coefficients and—what is more important—in the final state vibrational energy terms<sup>19</sup> for the different systems are small enough to be accounted for by the errors involved in their determination together with the fact that the coefficients and energy terms contain small contributions (I, p. 132) which differ from one system to another, due to the fact that the data refer to heads. The agreement is least good in the B system, where the reliable data are fewest. Granting that all five CuI band systems have the same final electronic state, it would seem that there is something peculiarly stable or normal about this state. There can, in fact, in view of the ready excitation of these bands and no others in the comparatively low temperature of the Bunsen flame,<sup>3</sup> taken together with the fact that they involve

<sup>18</sup> On p. 212 of Konen's book<sup>4</sup> the copper halide spectra are classed as "Pseudokanten-spektra" because the band heads become less and less conspicuous with increasing dispersion and in many cases finally disappear. On account of this behavior, Konen apparently considers it very doubtful whether the heads are genuine. The present analysis shows that the arrangement of the heads is completely in agreement with that found in other typical cases where no such question has been raised, and with that predicted by the quantum theory; also, the requirements of the isotope effect are completely satisfied. Hence the heads must be considered genuine. Their marked loss of conspicuousness under high dispersion is probably due to the close packing of the heads. This must result in the presence together at most points in the spectrum of series of structure lines from a number of different heads. When, under high dispersion, these are well resolved, the positions of individual heads, where new series begin, are naturally relatively inconspicuous. This is true especially of high-temperature spectra (flame or arc), where the series are prolonged. In active nitrogen the series are usually very short, corresponding to the low actual temperature. This tends to make the heads stand out much more sharply.

<sup>19</sup> The agreement is best brought out by comparing vibrational energy terms  $E''^n$ . These can be obtained from the original data or conveniently calculated from the equations of Table 6. Even for the larger values of  $n''$ , where  $E''^n = 2000$  to 4000 wave-number units, the maximum discrepancy between the energy terms for different systems is 4 units,—provided the comparison is restricted for each system to values of  $n''$  for which bands were actually measured.

initial state energies up to 3 volts in excess of the energy of the final state, be little doubt that this common final state is the normal state of the CuI molecule.

The near-equality of the  $n'$  coefficients for the A and D bands may be fortuitous or may indicate a relation between the two initial electronic states involved. The same is true in regard to the C and E bands. The agreement, it should be noted, does not extend to the coefficients of  $n'^2$ , at least in the latter case (in the former case the data are inadequate for decision).

The D bands are remarkable in that  $n'$  has only the values 0 and 1.<sup>20</sup> Presumably higher values of  $n'$  would involve instability of the molecule for the D electronic configuration.

In Fig. 2 the various electronic and vibrational levels revealed by the preceding analysis for Cu<sup>63</sup>I are arranged on a vertical wave-number scale; the arrangement is like that previously used in the case of BO.<sup>17</sup> At the right, the electron levels ( $N_0, A_0, \dots, E_0$ ) and their separations, are indicated. It should be recalled that the plotted values for the levels probably deviate slightly from the true values because the data used refer to heads. For Cu<sup>65</sup>I (not shown), the various electron levels coincide with those of Cu<sup>63</sup>I, but each set of vibrational levels has a somewhat smaller spacing, in accordance with the equations of Table VI.

It will be noted that in all five CuI systems the vibration frequency is less for the excited than for the normal electronic state. Although the individual bands are not resolved, the fact that they are all shaded toward the red is enough to show (cf Sommerfeld, *Atombau und Spektrallinien*, 4th ed., chap. IX, §3) that the interatomic distance and moment of inertia are greater, in all five systems, for the excited state than for the normal state of the molecule. The above facts both indicate weaker binding forces for the excited electronic states than for the normal state of CuI. The CuBr and CuCl bands disclose analogous relations for these molecules. The correlation of increased moment of inertia with decreased vibration frequency (or vice versa) when a molecular electron is excited is, as Birge has pointed out, a rule without known exception.<sup>21</sup>

*Analysis of CuBr and CuCl Spectra.* Most of the strongest CuCl heads (mostly the first head of each group) were arranged by Derichsweiler<sup>5</sup> in two long series (I and II) of approximately equally spaced heads. The same is true of CuBr. In each series the intensity is somewhat

<sup>20</sup> There are one or two doubtful and very weak bands for which, possibly,  $n' = 2$ .

<sup>21</sup> R. T. Birge, paper before American Physical Society (abstract No. 23, *Phys. Rev.* **25**, 240, 1925). The question of intensity distribution with respect to  $\Delta n$  and to  $n'$  was also discussed in this paper.

undulating, with two principal maxima. Corresponding members of series I and II form characteristic pairs of heads. In the case of CuI (cf. Table VII below), according to Derichsweiler, series II is nearly absent. The present analysis shows that Derichsweiler's arrangement into series has very little significance. In reality the spectrum of CuBr consists probably of four, that of CuCl of six (one closely double) different systems of bands, in part closely intermingled, giving rise to the appearance of pairs of heads.<sup>18</sup> Preliminary study indicates that, as with CuI, the several systems of each compound have a common final state.

#### CONFIRMATION OF VIBRATIONAL ISOTOPE EFFECT

In the reproductions of Plate I, practically all the Cu<sup>63</sup>I heads recorded in Tables I-V are marked. The corresponding weaker Cu<sup>65</sup>I heads are not marked, but many of them can be located by comparison with the tables. It will be seen that they are arranged entirely as would be expected (cf. theoretical diagram, I, p. 129). The Cu<sup>65</sup>I bands are especially well shown at the low-frequency end of the A system. In the region near the origin of each system, the heads of the two isotopes are of course not resolved. On the high-frequency side of the origin, the Cu<sup>65</sup>I heads are partially or wholly obscured, each by the shading from the adjacent Cu<sup>63</sup>I head.

In order to consider the question quantitatively, let us suppose that one of two isotopic molecules emits a system of bands, the wave-numbers of whose origins can be expressed by an equation of the form

$$\nu_1 = \nu^e + a'n' - b'n'^2 - a''n'' + b''n''^2 \quad (1)$$

Then for the other isotope, according to theory (I, p. 127),

$$\nu_2 = \nu^e + \rho a'n' - \rho^2 b'n'^2 - \rho a''n'' + \rho^2 b''n''^2 \quad (2)$$

Here  $\rho = \sqrt{\mu_1/\mu_2}$ ,  $\mu_1$  and  $\mu_2$  being the respective reduced masses. In case one has data on band-heads, instead of on origins, small contributions are added to all the terms of Eq. (1); and since these are subject to the *rotational* isotope effect, which differs from the vibrational effect, the relation of  $\nu_2$  to  $\nu_1$  is slightly altered. In respect to the terms depending on  $n'$  and  $n''$ , the effect should be negligible (I, p. 132) as compared with experimental error. In respect to the constant term, a small but perhaps appreciable effect is to be expected.<sup>22</sup>

<sup>22</sup> The fact that the data of Tables I-V are on heads, instead of on origins, involves the possibility of a slight shift of all the Cu<sup>65</sup>I heads with respect to the Cu<sup>63</sup>I heads. For the constant term of Eq. 1 now represents not  $\nu^e$  alone (for which no appreciable isotope effect is to be expected: (I, p. 124-5)), but  $\nu^e + \nu_{head}$ , where  $\nu_{head}$  is the distance from the origin to the head of the band for which  $n'$  and  $n''$  are both zero. Corresponding to  $\nu_{head}$  there must be a rotational isotopic displacement of approximately  $(\rho^2 - 1)\nu_{head}$

If  $\nu_1$  refers of  $\text{Cu}^{63}\text{I}$ , then for  $\text{Cu}^{65}\text{I}$  as compared with  $\text{Cu}^{63}\text{I}$ ,  $\rho = 0.98966$ , and  $\rho^2 = 0.97943$ . From the  $\text{Cu}^{63}\text{I}$  coefficients in the equations of Table VI, the corresponding theoretical values of the  $\text{Cu}^{65}\text{I}$  coefficients can be calculated. The equations so obtained have been given in Table VI. From these the theoretical positions of all the  $\text{Cu}^{65}\text{I}$  heads can be calculated. These predicted values can then be compared with the experimental data. It is most convenient to do this by comparing calculated with observed values of the *isotopic displacement*,  $(\nu_2 - \nu_1)$ , as is done in Tables I-V. The result is complete agreement, within experimental error, for the entire range of  $n'$  and  $n''$  values in all the systems, so far as data could be obtained.<sup>22,23</sup> The slight average deficiency in the observed as compared with the calculated isotopic displacements for the E bands is probably within experimental error, but is in the direction to be expected<sup>22</sup> from the fact that the measurements were on heads. The data are not accurate enough to furnish evidence on the question of half-integral vibrational quantum numbers.<sup>22</sup>

#### INTENSITY DISTRIBUTION IN THE CUI BANDS

In a system of bands, the distribution of intensity with respect to  $n'$  and  $n''$  is of interest chiefly from two points of view, distribution with

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(I, p. 131). In the CuI bands,  $\nu_{\text{head}}$  is always positive, since the heads are shaded toward the red. Hence, since  $(\rho^2 - 1)$  is negative here, this rotational contribution to  $(\nu_2 - \nu_1)$  must be negative; its magnitude, of course, cannot be determined without analysis of the band structure. In the equations of Table VI and the calculated isotopic displacements of Tables I-V, no allowance was made for this contribution. If it is appreciable, it should therefore be evident by an appreciable negative value for the average observed minus the average calculated isotopic displacement.

If, as is apparently true in BO,<sup>17</sup> the true minimum values of  $n'$  and  $n''$  are 1/2 instead of 0 as assumed throughout the preceding discussion, the bands here assumed to have  $n' = n'' = 0$ , and so the constants of the equations of Table VI, should be subject to a vibrational isotopic displacement  $(\nu_2 - \nu_1)$  of +0.28 units for the A bands, and +0.18 units for the E bands. These effects are accordingly of opposite sign to the rotational head effect discussed in the preceding paragraph. The calculated net effects should be: A bands, +0.28 - x; E bands, +0.18 - y. The observed effects are: A bands, +0.05; E bands, -0.4. It will be seen that the observed effects do not contradict the existence of half quantum numbers. The relatively large experimental error, the possibility of relative error, due to differences in intensity, etc., in setting on the heads of the two isotopes, and the fact that x and y are unknown, make it impossible, however, to draw any positive conclusions.

<sup>23</sup> The confirmation of the theory is of course not nearly as exact as in the case of BO,<sup>17</sup> on account of the much smaller values of the isotopic displacements.

In the case of BO, equations for  $\nu_1$  and  $\nu_2$  were obtained independently from the experimental data, and their coefficients compared. This is a rather more rigorous test than that here applied; but unless the data used are equally complete and accurate for both isotopes, it is one which is likely to disguise somewhat the real agreement with theory.

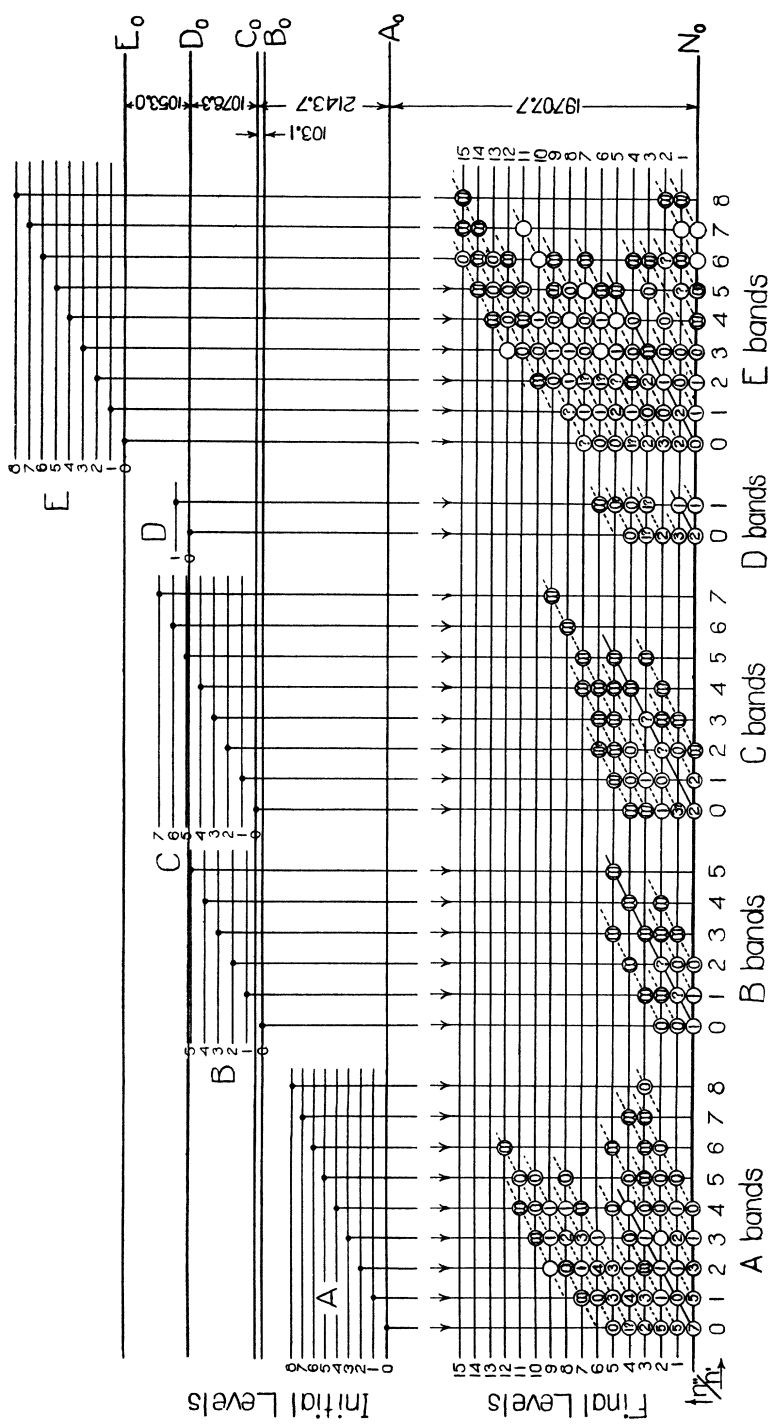


Fig. 2. Energy level diagram for CuI molecule.

Fig. 2. Energy level diagram for CuI molecule.—The electronic and vibrational energy levels found by analysis of the CuI band spectrum are shown on a vertical wave-number scale. Each electronic level ( $N_0$ , the normal level,  $A_0, B_0, \dots$ , excited levels) is shown by a heavy horizontal line; above it the correlated vibrational levels are shown. In the case of the excited electronic states, the lines for the vibrational levels are drawn only part way across the diagram, in order to avoid confusion. Rotational levels are not shown. The A bands correspond to transitions from A levels to N levels, the B bands to transitions from B to N levels, and so on. Each observed band is indicated by a circle near the lower end of a vertical line, the figure in the circle denoting intensity; where the figure is omitted, the intensity is very low (000). Diagonal lines are used to indicate band-sequences, the full-line diagonal representing the (0) sequence. The spacing of the electron levels is indicated at the right.

respect to  $\Delta n$  ( $\Delta n = n'' - n'$ ), and with respect to  $n'$ . The former is a matter of transition probability, depending on several factors recently discussed by Lenz in relation to the correspondence principle.<sup>24</sup> The latter probably depends chiefly on the initial distribution of excited molecules among various  $n'$  values, and so gives a means of studying the  $n'$  distribution. In the case of CuI, Fig. 2 gives a good idea of these distributions for each of the five systems of bands. Each diagonal line serves to mark out a "band-sequence," i.e., a set of bands of given  $\Delta n$ ; each vertical line marks a set of given  $n'$ . By comparison of adjacent diagonal or vertical sets, respectively, the  $\Delta n$  or  $n'$  distribution can be studied.

For thermal equilibrium, the number  $N_n$  of molecules having a given value  $n$  of the vibrational quantum number  $n'$ , and a corresponding energy  $E_n$ , should be proportional to  $e^{-E_n/kt}$ . Assuming, as an approximate average value for the five systems,  $E_n = 225n$  (wave-number units), taking  $k$  in the same units ( $k = 0.698$ ), and assuming  $T = 373^\circ\text{K}$ ,  $N_n$  is proportional to  $e^{-0.865n}$ . For  $n = 0, 1, 2, 3, 4, 5, \dots$  this gives values of  $N_n$  proportional to 1, 0.42, 0.177, 0.075, 0.032, 0.013,  $\dots$ . No more than a rough qualitative comparison is possible with the recorded intensities of Tables I-V and Fig. 2. However, it will be seen that in all five systems there is a steady falling off of intensity from  $n' = 0$ —except, as previously noted, that the  $D$  bands are completely cut off above  $n' = 1$ —at a rate which seems to be in accord with the preceding calculations, corresponding to a low temperature.

The above result is in contrast to that previously observed<sup>17</sup> in the case of the  $\alpha$  and  $\beta$  systems of BO. For BO,  $E_n$  is approximately  $1260n$ , so that the  $N_n$  values should fall off very rapidly, in proportion to  $e^{-4.85n}$  for equilibrium at  $100^\circ\text{C}$ . For  $n' = 0, 1, 2, \dots$  they should then be proportional to 1, 0.0079, 0.00006,  $\dots$ . Actually, the  $n' = 0$

<sup>24</sup> W. Lenz, *Zeits. f. Phys.* **25**, 299 (1924). Cf also T. Heurlinger, *Zeits. f. Phys.* **1**, 82 (1920).

series are less intense than some of the others, the intensity maximum being near  $n' = 2$ ; in addition, bands with  $n'$  values as high as 8 were observed, which would obviously be impossible for thermal equilibrium. Non-thermal and high-temperature vibrational energy distributions occur in other cases of band spectra excited by active nitrogen, e.g., in the CN and SiN bands. In the case of the NO  $\beta$  bands ( $\beta$  bands of active nitrogen), as Birge has recently pointed out,<sup>21</sup> the distribution corresponds more nearly to equilibrium at the (low) temperature of active nitrogen. Further discussion of these points will be found in the paper<sup>17</sup> on BO.

The distribution with respect to  $\Delta n$  in the CuI bands considerably resembles that in the  $\beta$  bands of BO.  $\Delta n$  ranges from perhaps  $-6$  to  $+9$ , and, although there is some approach to the symmetry about  $\Delta n = 0$  which is predicted by Lenz's theory,<sup>24</sup> there is an obvious preference for positive  $\Delta n$  values.<sup>25</sup> Another characteristic feature, noted here and in both  $\alpha$  and  $\beta$  systems of BO, and perhaps typical of band spectra in general,<sup>21</sup> is the tendency for numerically large  $\Delta n$  values to be associated with large  $n'$  values. Although Lenz does not refer to it, this effect, as also the preference for positive  $\Delta n$  values, appears to be predictable from his theoretical treatment; for the occurrence of large values of  $\Delta n$  is there connected with the existence of considerable perturbations of the electronic motion by the vibrational motion of the nuclei; and the magnitude of such perturbations must increase with the value of  $n$ , which determines the amplitude of vibration. Hence large values of  $n'$  should favor large values of  $\Delta n$ , and also, since the motion of the emitting electron in both initial and final states of the molecule must be considered in Lenz's application of the correspondence principle, should favor positive values of  $\Delta n$ , since for these  $n''$  is also large.

The association of large  $n'$  with large  $\Delta n$  values has a striking effect on the appearance of band sequences in cases, like those of the copper halides, where the members of a sequence follow one another in close succession (cf. Plate I). In the sequences near the origin, i.e., those for which  $|\Delta n|$  is small, each sequence begins with an intense head—for which either  $n'$  or  $n''$  is zero—the succeeding heads being progressively less intense.<sup>26</sup> Farther from the origin, the intensity maxi-

<sup>25</sup> This is probably *not* due primarily to variations in plate sensitivity and prism transmission, although of course these must have a marked distorting influence.

<sup>26</sup> Exceptions to this rule of progressive decrease sometimes occur due to abnormally low intensity of particular bands. Thus (cf. Plate I) the  $\Delta n = 0$  sequence of the E bands starts out with a weak (0,0) head, while the  $\Delta n = +1$  sequence has a weak spot at the (1,2) band; again, the A sequence for which  $\Delta n = 0$  has a weak spot at (1,1), followed by a revival with (2,2).

mum shifts away from the first head, and in the highest-numbered sequences the first few heads may become too weak to be detected (cf. Plate I and Fig. 2, A and E bands). Konen noted this effect in the copper halide bands, and gives a good diagram<sup>4</sup> illustrating it in the case of some of the CuCl bands; certain fluoride bands also show it well. This phenomenon is particularly well marked in the positive sequences ( $\Delta n$  positive). Here the first head of each sequence corresponds necessarily to  $n' = 0$ , whereas in the negative sequences, the value of  $n'$  for the first head is necessarily the same as  $|\Delta n|$ .

Attention may be called to the A bands of CuI as a typical example, with respect to arrangement and intensity distribution, of a well-developed band system. The A bands also illustrate well the abrupt change of spacing for the strong first heads of successive sequences, at the origin of the system. These points appear to good advantage in Plate I on account of the freedom from marked variation of photographic sensitivity and from overlapping by other band-systems, in the region occupied by the A bands. The absence of resolution of the bands into structure lines also helps to make clear the arrangement of the bands.

#### COMPARISON WITH DATA OF PREVIOUS INVESTIGATORS

Data in the literature on complex band spectra often refer to the first head only of each of the more obvious sequences. This is illustrated in Table VII, where the data of previous observers on the CuI bands are

TABLE VII

*Comparison with previous data*

Previous data (wave-lengths)*			Present identification
M.	D.	E.&V.	
5393	—	—	A sequence 5354-5419
5314	—	5330	" " 5282-5364
—	—	5250	?
5232	—	—	A sequence 5211-5241
—	5210(I)	5210	Head 0,2 A, 5210.7
5144	5141(I)	5142	" 0,1 A, 5141.1
—	—	5106	" 2,2 A, 5101.9
5073	5072(I)	5075	" 0,0 A, 5072.8
5018	5019(II)	—	" 1,0 A, 5019.7
4959	—	—	" 2,0 A, 4968.3(?)
—	4883(II)	—	A sequence 4873-4930
—	4826?(II)	—	?
—	4769(II)	4760	C sequence 4744(?)
—	4710(II)	—	Head 0,2 B, 4711.3
—	4686(I)	4685	" 0,2 C, 4686.8 and 4687.8
—	4631(I)	4630	" 0,1 C, 4630.6
—	4575(I)	4575	" 0,0 C, 4575.2

\* M. = Mitscherlich (wave-lengths calculated by Watts in his "Index of Spectra" from photograph by Mitscherlich); D. = Derichsweiler (Roman numerals in parentheses after wave-lengths denote series of Derichsweiler<sup>5</sup>); E. & V. = Eder and Valenta.<sup>3</sup>



TABLE VII—continued

4523(I)	4523	Head 1,0 C, 4527.9
4462(?) (I)	4464	" 0,2 D, 4462.2, and 1,7 E, 4463.6
4409(I)	4408	" 0,5 E, 4408.1
4358(I)	4358	" 0,4 E, 4358.3; 0,0 D, 4360.0; 1,5 E, 4364.0
—	4323	?
—	4320	" 1,0 D, 4320.0
4309(I)	—	" 0,3 E, 4308.2 and 4309.6
—	4280	" 3,5 E, 4280.1
4261(I)	4261	" 0,2 E, 4261.7
4214(I)	4213	" 0,1 E, 4214.6
4169(I)	4172	" 0,0 E, 4168.5 or 1,1 E, 4174.6
4126(I)	4130	" 1,0 E, 4129.4
—	4098	" 2,0 E, 4091.3

compared with the present data. In the higher-numbered sequences, the first head becomes too faint to be noticed, and a rough measurement of the beginning or middle of the region of maximum intensity is likely to be given; obviously such data are of almost no value from a theoretical standpoint.

For the first head of a sequence, either  $n'$  or  $n''=0$ . On the low-frequency side of the origin ( $n', n''=0$ ), in each CuI system, these form a series ( $n', n''$ ) = (0, 0), (0, 1), (0, 2), . . . with a nearly constant first difference of somewhat over 260 wave-number units, common to all five systems on account of their common final electronic state. Derichsweiler's series I for CuI is made up chiefly of the E bands (0, 0), (0, 1), . . . (0, 5) and the C bands (0, 0), (0, 1), (0, 2), pieced together by (0, 2) D and (1, 0) C, which, however, of course do not fit in very well (this was explained by Derichsweiler as perhaps due to inaccuracies of measurement). After a gap containing miscellaneous bands grouped as series II, series I reappears with (0, 0), (0, 1), and (0, 2) of the A system.

#### THE EXCITATION OF SPECTRA BY ACTIVE NITROGEN

The suggestion has been made by several writers<sup>27,28,29</sup> that the excitation of spectra by active nitrogen is the result of "collisions of the

<sup>27</sup> R. T. Birge: cf. abstract, Phys. Rev. **23**, 295 (1924); Nature, Nov. 1, 1924.

<sup>28</sup> R. S. Mulliken, loc. cit.;<sup>7</sup> Nature, Sept. 6, 1924; Phys. Rev. **25**, 278 (1925).

<sup>29</sup> M. N. Saha and N. K. Sur, Phil. Mag. **48**, 421 (1924). It should be pointed out that this paper contains certain errors in the interpretation of the band spectra appearing in active nitrogen, and in the estimated energy of the latter. These have been corrected in Birge's letter<sup>27</sup> to Nature. See also Foote and Ruark, Nature, Nov. 22, 1924, and Foote, Ruark, and Chenault, (abstract, Phys. Rev. **25**, 241, 1925) who discuss the excitation of the spectrum of mercury by active nitrogen. The present writer believes that Birge's estimate of about 11.5 volts, for the energy of active nitrogen in the state which immediately precedes the emission of the characteristic visible afterglow bands, should be reduced to 10.4 volts (this point will be discussed elsewhere). The true energy may be somewhat different, however, probably higher, since the active nitrogen must be in a metastable state<sup>27</sup> which presumably differs from the emitting state, although Birge assumes the two to be identical.

second kind," analogous to the action of excited mercury atoms in the work of Franck and Cario.<sup>30</sup> The effects are, however, much more varied in active nitrogen than with excited mercury atoms. The excitation of atomic spectra by active nitrogen, as studied experimentally by E. P. Lewis<sup>31</sup> and by Rayleigh and Fowler,<sup>32</sup> has been discussed in some detail by Saha and Sur.<sup>29</sup>

The behavior of the copper halides in active nitrogen illustrates particularly two characteristic modes of action of the latter. As indicated in the preliminary abstract,<sup>7</sup> it appears that excited  $N_2$  molecules may either (a) excite molecular electrons so as to give rise to the emission of the halide band spectra, or (b) dissociate the halide molecules. The excitation of atomic spectra is also illustrated, excitation of the copper and halogen atoms possibly accompanying but probably following the dissociation. Another possibility referred to in the abstract, namely reaction with the halide molecule to form copper nitride, must now be regarded as very doubtful (see under "oxide bands" in introduction), although the analogous process occurs in many other cases, e.g.,<sup>33</sup> formation of CN and SiN, respectively, by reaction of  $N_2'$  molecules (the prime will be used to denote an excited atom or molecule) with carbon and silicon compounds. Other interesting reactions are the appearance of the NO bands<sup>33</sup> on admission of  $O_2$  or other oxygen compounds into active nitrogen, and of the CN and NO bands (also probable CO bands) on admission of CO. Possible formulations of these reactions are  $O_2 + N_2' \rightarrow NO' + NO$ , and  $CO + N_2' \rightarrow CN' + NO$ , or  $CN + NO'$ .

In the case of the copper halides, the occurrence in high intensity of the copper arc spectrum (over 80 lines were identified) and of the intense iodine arc line<sup>34</sup> at  $\lambda 2062$  when CuI was used, indicate that excited Cu

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The subject of active nitrogen has also been discussed by N. R. Dhar (J. Phys. Chem. **28**, 948, 1924).

<sup>30</sup> Franck and Cario, Zeits. f. Physik **9**, 259; **10**, 185; **11**, 161 (1922); **17**, 202 (1923).

<sup>31</sup> E. P. Lewis, Astrophys. J. **20**, 49 and 58 (1904); Phil. Mag. **25**, 826 (1913); and other papers.

<sup>32</sup> Ref. 10 and later papers in Proc. Roy. Soc.

<sup>33</sup> See R. S. Mulliken, Phys. Rev. **25**, 277-8, 290, and references there cited.

<sup>34</sup> C. Füchtbauer, F. Waibel, and E. Holm found this line strongly absorbed in atomic iodine at 1000°C (Zeits. f. Phys. **29**, 367, 1924). Their measured wave-length was  $\lambda_{vac.} = 2062.1 \pm 0.1$ . An approximate measurement by the writer on the emission line obtained from CuI gave  $\lambda_{vac.} = 2062.3$ . W. Gerlach and F. Gromann (Naturw. **12**, 578, 1924) had previously reported a line at  $\lambda 2063$  absorbed by partly dissociated iodine at 150°C, but their result is less conclusive than Füchtbauer's on account of the probable molecular absorption. A strong emission line at  $\lambda 2064$  reported by O. Oldenberg (Zeits. f. Phys. **18**, 7, 1923), and at  $206m\mu$  by Ludlam and West (Nature **113**, 389, 1924), is without doubt identical with that here under discussion. The nature of  $\lambda 2062$  has also been discussed recently by L. A. Turner and K. T. Compton (Phys. Rev. **25**, 791, 1925).

and I atoms are formed in large numbers as a direct or indirect result of process (b) above. Exactly the same set of Cu lines is obtained, with the same relative intensities, so far as could be judged from inspection of the photographs, whether CuCl or CuI is used (and so far as could be seen in a short exposure, the same as with CuBr). According to Dr. A. G. Shenstone, who was so kind as to examine the data, the entire arc spectrum appears to be present, and in addition a group of lines whose initial state corresponds to a slightly negative term, hence presumably to simultaneous excitation of two electrons. The spectrum differs markedly in intensity distribution from that of the ordinary copper arc.

It may be noted that there was no trace, when CuI was used, of the intense band spectrum which is excited when iodine ( $I_2$ ) is admitted to active nitrogen.

Since CuCl is known to be largely or completely associated to  $Cu_2Cl_2$  in the vapor state<sup>35</sup> (presumably CuBr and CuI also are associated), it is not possible at present to specify definitely the details of processes (a) and (b) above. It is likely that the formation of  $CuX'$  molecules and  $Cu'$  and  $X'$  atoms by the interaction of  $N_2'$  molecules and  $CuX$  or  $Cu_2X_2$  molecules occurs in a number of different ways. The category of possible modes of dissociation and excitation is of course limited to processes in which the expenditure of energy does not exceed the initial energy of the  $N_2'$  molecule (plus a small contribution due to energy of relative translation of the impinging molecules); this initial energy corresponds probably to 10.4 volts or a little more.<sup>29</sup>

The formation of  $CuX'$  molecules might occur directly from  $Cu_2X_2$  and  $N_2'$ , or might require the intermediate formation of unexcited  $CuX$  molecules. Similarly the formation of Cu and X atoms from  $Cu_2X_2$  might occur in one or in two steps, and the formation of  $Cu'$  and  $X'$  atoms in from one to three steps. In any case there are three distinct possibilities as to the mode of excitation of the Cu and X atoms: (1), the dissociation of  $Cu_2X_2$  or  $CuX$  molecules may yield neutral unexcited atoms, excitation of these occurring in subsequent impacts with  $N_2'$  molecules; (2), excitation may occur simultaneously with dissociation; (3), the dissociation may yield the ions  $Cu^+$  and  $X^-$ . Since the ionization potential of Cu is about 7.7 volts, the energy of  $N_2'$  is considerably more than enough for the excitation of the entire arc spectrum of Cu in secondary impacts of Cu with  $N_2'$  in connection with (1); further, the excited spectrum should be the same for all three halides, as is the case for the observa-

<sup>35</sup> See von Wartenberg and Bosse, *Zeits. f. Elektrochem.* **28**, 384 (1922).

tions reported above. In process (2) the energy required includes a heat of dissociation in addition to the energy of excitation. The heat of dissociation may be estimated<sup>36</sup> at 2 or 3 volts for CuX, so that excitation of the entire arc spectrum might still be possible. It would, however, be strange if there were not then differences in intensity distribution, contrary to the observed facts, for the different halides. Dissociation of  $\text{Cu}_2\text{X}_2$  in any manner, with simultaneous excitation of Cu atoms to give the entire arc spectrum, must probably be ruled out on account of the large energy required for dissociation.<sup>36</sup> Process (3), followed by reunion of an electron with a  $\text{Cu}^+$  ion, should like process (1) give the same Cu spectrum for all the halides, in accord with observation. The energy required for (3) would not be excessive<sup>37</sup> for dissociation of CuX, but might be too great for the reaction  $\text{Cu}_2\text{X}_2 \rightarrow \text{CuX} + \text{Cu}^+ + \text{X}^-$ . On the whole, the evidence is decidedly against (2), and in favor of (1) or (3), as the main factor in the formation of excited Cu atoms. Energy considerations favor (1) as against (3) if the dissociation of  $\text{Cu}_2\text{X}_2$  occurs in one step; the fact that the system  $\text{Cu} + \text{X}$  has less energy than  $\text{Cu}^+ + \text{X}^-$  also indicates it to be a more likely result of dissociation. For the formation of X' atoms only (1) is possible.

The increasing relative intensity of the Cu line spectrum, as compared with the CuX band spectrum, in going from CuCl to CuI, may be ascribed to an increasing probability of dissociating rather than exciting the CuX molecule, correlated with the decreasing chemical stability of the molecules in this order.

There is a possibility that  $\text{CuX}_2$  molecules may be important in the excitation of the spectra of the Cu halides by active nitrogen, although

<sup>36</sup> Assuming that all three cuprous halides are present in the vapor state chiefly as double molecules, the following approximate values for the heat of dissociation into unexcited neutral atoms can be calculated from thermochemical<sup>35</sup> and electron affinity data:  $\text{Cu}_2\text{Cl}_2$ , 10.2 volts,  $\text{Cu}_2\text{Br}_2$ , 9.1 v,  $\text{Cu}_2\text{I}_2$ , 8.3 v, using the value 68 kg.-cal. per mol for the heat of vaporization of Cu (cf R. W. Millar, *Ind. Eng. Chem.* **17**, 34, 1925). The heat of dissociation of CuX into atoms and of  $\text{Cu}_2\text{X}_2$  into 2 CuX are unknown, but may be estimated by assuming that the former is the same as for AgX (which does not form double molecules in the vapor state). The writer is indebted to Dr. R. H. Gerke for this suggestion. For AgCl vapor, the heat of dissociation into atoms is equivalent to about 3.3 volts, for AgI to about 2.2v (cf. R. H. Gerke, *J. Am. Chem. Soc.* **46**, 953, 1924; also von Wartenberg and associates, *Zeits. f. Elektrochem.* **27**, 162, 568, 1921, and **28**, 284, 1922). Assuming the same values for CuCl and CuI, the heat required for  $\text{Cu}_2\text{X}_2 \rightarrow 2\text{CuX}$  is then equivalent to 3.6v for CuCl and 3.9v for CuI.

<sup>37</sup> Gerke (l.c.<sup>36</sup>) points out that for halogen salts the heat of dissociation is approximately equal to the electron affinity of the halogen. A corollary of this is that the heat of dissociation of such salts into ions must be about equal to the ionizing potential of the metal.

the weight of chemical evidence indicates that  $\text{CuX}_2$  is decomposed to  $\text{Cu}_2\text{X}_2$  and  $\text{X}_2$  in the process of vaporization. In the present work, both  $\text{CuCl}_2$  and  $\text{Cu}_2\text{Cl}_2$  were used, but no obvious differences in relative intensities of different bands, or of the bands as compared with the Cu lines, were observed.

*Mercury halides.* Some experiments of the writer on the excitation of spectra of certain volatile salts by active nitrogen are of interest here.  $\text{PbI}_2$ ,  $\text{HgI}_2$ , and  $\text{HgBr}_2$  have been tried.<sup>38</sup> Each gives the arc spectrum of the metal, well developed, also  $\lambda 2062$  and other I arc lines<sup>38</sup> in the case of the iodides, and characteristic halide bands in each case (very weak in the case of  $\text{PbI}_2$ , strong in the other two cases). The band spectra appear to be rather complex, suggesting triatomic emitters  $\text{MX}_2$ , but it seems more likely that they are due to diatomic emitters  $\text{MX}$ , in which case the complexity may be due to the presence of several superposed systems of bands as in the  $\text{CuX}$  spectra. In the case of the two Hg salts, the complete arc spectrum of Hg appears to be developed; thus diffuse series lines are present at least up to  $2p_1-6d$ ; the  $6d$  terms correspond to an energy of 10.0 volts, only 0.4 v short of ionization. In both cases the intensity distribution appeared to be closely similar to that in other experiments where Hg alone was used (except that  $\lambda 2537$  was relatively much weaker in the latter case, presumably because of greater absorption).<sup>38</sup> These results parallel those with  $\text{CuCl}$  and  $\text{CuI}$ , and lead to similar conclusions, except that process (1), dissociation into unexcited atoms, is even more definitely indicated here, on account of the high ionizing potential of Hg, as the chief factor. The formation of  $\text{Hg}^+$  ions, probably by the reaction  $\text{Hg} + \text{N}_2' \rightarrow \text{Hg}^+ + \text{N}_2 + e$ , is indicated by the (rather weak) presence of the Hg spark line  $\lambda 1942$  (the emission of this line would follow the secondary process  $\text{Hg}^+ + \text{N}_2' \rightarrow \text{Hg}^{++} + \text{N}_2$ ).

The study of the excitation of spectra by active nitrogen is being continued, and a further discussion will be given later.

<sup>38</sup> In some of the experiments with the iodides, the characteristic banded structure beginning near  $\lambda 3450$ , which results<sup>10</sup> from the action of  $\text{N}_2$  (or a suitable electrical discharge) on  $\text{I}_2$ , was present. This was probably due to partial decomposition of the iodide before its entrance into the active nitrogen, or in part to secondary formation of  $\text{I}_2$  from I atoms, rather than to direct formation of  $\text{I}_2$  or  $\text{I}_2'$  molecules by dissociation. The spectrum of  $\text{HgI}_2$  in active nitrogen was earlier examined by Rayleigh and Fowler<sup>10</sup>, who found this iodine band fairly prominent. Of the Hg line spectrum, they noted only  $\lambda 2537$ ; this result was probably due to an exposure insufficient to bring out the other lines, since in the present work  $\lambda 2537$  was found to be much more prominent than the latter.—In the present work with the iodides (and iodine) several additional lines, evidently iodine arc lines, were noted (cf. abstract of paper by R. S. Mulliken and L. A. Turner, *Phys. Rev.* **25**, 886, 1925).

NATURE OF EXCITED ELECTRONIC STATES IN COPPER HALIDE  
MOLECULES, AND THE BAND SPECTRA OF  
POLAR COMPOUNDS

The nature of the electronic changes involved in the excitation of the CuX molecule (X=any halogen) will now be considered briefly. Since CuX is of a polar or ionic type—although less definitely so than compounds like NaCl—the excited electron must probably belong either to the Cu<sup>+</sup> ion or to the X<sup>-</sup> ion. Excitation of an X<sup>-</sup> electron in Cu<sup>+</sup>X<sup>-</sup> by impact with a free electron or excited atom or molecule would presumably mean complete loss of this electron to the Cu<sup>+</sup> ion, since outer quantized orbits are hardly to be expected for this electron in the X<sup>-</sup> ion. The Cu atom would thus be left in its normal state, or, if enough energy were supplied, in one of several excited states; and the Cu and X atoms would be left clinging together by virtue of secondary forces as a non-ionic molecule CuX. From this condition they might undergo, as the result of the impact of a third molecule, either the change CuX→Cu+X, or (cf. Born and Franck, ref.<sup>39</sup>) CuX→Cu<sup>+</sup>X<sup>-</sup>. The spontaneous occurrence, with the emission of a band spectrum, of the reaction CuX or Cu<sup>+</sup>X<sup>-</sup>→Cu<sup>+</sup>X<sup>-</sup> is conceivable, but must probably be ruled out.<sup>39</sup> Another possibility is that, in the presence of a Cu<sup>+</sup> ion, the I<sup>-</sup> ion would be so greatly deformed that a series of quantized states for an I<sup>-</sup> electron could occur, resembling those in an I atom. It is more probable, however, that the observed group of five electron levels in the CuI molecule corresponds to excitation of the Cu<sup>+</sup> ion. The five CuI band-systems should then be analogous to the most easily excited lines of the Cu<sup>+</sup> spectrum. This spectrum should contain odd-numbered multiplets. The group of CuI levels A<sub>0</sub> to E<sub>0</sub> might then correspond to a multiple term of Cu<sup>+</sup>, considerably modified, of course, and perhaps increased in complexity, by the presence of the I<sup>-</sup> ion.

That the Cu<sup>+</sup> ion contains an easily excited electron or electrons is indicated by the existence of salts in which the Cu atom has a valence of two, showing that the Cu<sup>+</sup> ion in Cu<sup>+</sup>X<sup>-</sup> has an electron which is easily transferred to a halogen atom to form Cu<sup>++</sup>X<sup>-2</sup>. The process of complete transfer of a Cu<sup>+</sup> electron to an X atom is of course markedly different from the mere excitation of a Cu<sup>+</sup> electron in Cu<sup>+</sup>X<sup>-</sup>; it may be described as an induced ionization, being assisted by the electron affinity of the X

<sup>39</sup> M. Born and J. Franck (Ann. der Physik, **76**, 229, 1925) have concluded that the emission of radiation in such a process is, on correspondence principle grounds, not to be expected. The same would apply to the converse process of excitation of the molecule by absorption of radiation. See also their important article in Zeits. f. Phys. **31**, 411 (1925).

atom. Excitation of a  $\text{Cu}^+$  electron in  $\text{Cu}^+\text{X}^-$ , and complete transfer as in  $\text{Cu}^+\text{X}^- + \text{X} \rightarrow \text{Cu}^{++}\text{X}^{-2}$ , stand, however, in much the same relation as excitation and ionization of an electron in a single atom. Since in general low ionization potentials involve low resonance potentials, the above correlation of  $\text{CuX}_2$  formation with  $\text{CuX}$  excitation seems justified.

In the same connection it is noteworthy that the halides of those metals which show a valence only of one give no electronic band spectra. In this class are the halides of the alkali metals (and hydrogen).<sup>40</sup> The absence of a valence of two in these cases must depend mainly on the absence of a low enough ionization potential for the positively charged ion ( $\text{M}^+$ ) of the metal. It is especially notable that silver, which belongs in the same group of the periodic system as copper but fails to show a valence of more than one, also fails<sup>40</sup> to give halide band spectra. Gold, also in the same group, shows valences of one and three, and gives halide spectra. It may be that in polar compounds the molecule is incapable of carrying electronic energy much in excess of the heat of dissociation into atoms, any attempt to impart larger amounts of energy resulting, either spontaneously, or as an indirect result of the formation of an excited molecule of a type highly sensitive to encounters with other molecules, in prompt dissociation.<sup>41</sup> The heat of dissociation into atoms corresponds to between 3 and 6 volts for the various alkali and hydrogen halides (being least for the iodides and for the hydrogen compounds), and probably to between 2 and 5 volts for the three cuprous halides.<sup>36,37</sup> The observed band systems of the Cu halides probably all correspond to electronic excitation energies lying between 2.4 and 3.1 volts;<sup>42</sup> for the five CuI systems the figures are 2.44, 2.68, 2.70, 2.83, and 2.96 volts. The complete absence of ultraviolet band spectra in the Cu halides, and of *all* electronic band spectra in the other halides mentioned, can both, then, be accounted for by the suggestion above in regard to instability of energized molecules.<sup>43</sup>

<sup>40</sup> There appears to be no record whatever in the literature of electronic band spectra for these compounds, in spite of much investigation.

<sup>41</sup> In the case of non-polar compounds such as  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{I}_2$  it is, however, of course well known that the molecule can possess electronic energy greatly in excess of the heat of dissociation, and can lose this excess energy in band spectrum emission.

<sup>42</sup> This is definitely shown for CuI by the preceding analysis, and is also probably true for CuBr and CuCl.

<sup>43</sup> A possible alternative explanation of the absence of observed band spectra in the compounds mentioned is that they lie wholly in or below the Schumann region. It seems unlikely, however, that this would be consistently true for all members of the class, and that, in addition, no jumps between higher levels would occur giving rise to bands in the visible or ordinary ultraviolet. Also, in recent unpublished work of Dr. L. A. Turner on a mixture of  $\text{H}_2$  and  $\text{I}_2$ , no bands attributable to HI were found in the Schumann region. The occurrence in positive rays of such ions as  $(\text{HCl})^+$ ,  $(\text{NaI})^+$ ,  $(\text{HgI}_2)^+$ , etc., suggests

If MX molecules are unable, on account of the absence of an easily excited electron in the ion  $M^+$ , to give electronic band spectra, one would naturally expect the same to be true of  $MeX_2$  molecules, where Me is one of the alkaline earth metals; for the  $Me^{++}$  ion, like the  $M^+$  ion, contains no easily excited electron.<sup>43</sup> As a matter of fact, all the members of this group give band spectra, in the visible and near ultraviolet, with ease; the fact that many of these can be obtained in the Bunsen flame shows that the electronic energy of the emitting molecule is relatively small, the band emission being in all probability accompanied by a return to the normal state of the molecule. These facts obtain a simple explanation in harmony with preceding considerations if one attributes these bands to compounds  $Me^+X^-$  present in small amounts. Such compounds contain one unused valence electron which should be very easily excitable, much like the single valence electron in an M atom. The excitation of MeX spectra by adding  $MeX_2$  to a flame would then be completely analogous to the excitation of M spectra by the addition of MX to a flame (e.g., the excitation of the sodium D lines by adding NaCl to a flame). There is little evidence for compounds of the type MeX in the solid state,<sup>44</sup> but their existence in the vapor state is to be expected, in small amounts in equilibrium with  $MeX_2$  and Me molecules. Such molecules would considerably resemble BO and CN (also SiN); all are "odd molecules" containing a single unused and presumably easily excited valence electron; it may be recalled that in a previous paper<sup>33</sup> considerable evidence was presented for the existence of an analogy between BO and CN and the Na atom. The structure of the spectra of the alkaline earth halides appears to be in agreement with the suggestion that they are due to diatomic molecules, although further investigation is needed. Also, these spectra are characterized by electronic doublets whose separation is of the same order of magnitude as, and which may well be analogous to, those of the spark spectra of the corresponding alkaline earth metals and of the arc spectra of the adjacent alkali metals.<sup>45</sup>

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of course, that these should give electronic band spectra, but it should be remembered that a molecule which has completely lost an electron may be stable even if the same molecule with this electron in a highly excited state is unstable.

<sup>44</sup> But cf. refs. given in J. W. Mellor's "Treatise on Inorganic and Theoretical Chemistry," Vol. III, p. 713; also cf. stability calculations by H. G. Grimm and K. F. Herzfeld, *Zeits. f. Phys.* **19**, 141, 1923.

<sup>45</sup> The spectra of the alkaline earth halides contain each apparently two or more band-systems. The spectra of the chlorides, bromides, and iodides of Ca, Sr, and Ba are closely homologous, as was shown by Olmsted (C. M. Olmsted, Dissertation Bonn, 1906; *Zeits. wiss. Phot.* **4**, 255-333, 1906). In each case Olmsted investigated particularly one complex system, of homologous structure and similar position for all these



The occurrence of MH,  $M_2$ , and similar spectra is not in contradiction with the preceding considerations, which deal with molecules of a polar type; for the types MH and  $M_2$  are probably analogous to the non-polar molecule  $H_2$  or are loose compounds whose electrons are bound in orbits which do not differ radically from those of the same electrons in the unshared atoms, so that these electrons are capable of being excited, with varying degrees of ease, without causing the molecule to become highly unstable.<sup>41,46</sup> The characteristic emission of band spectra by molecules of the supposedly polar type  $Me^{++}O^{--}$  is less readily explained, but may be ascribed to an approach to the non-polar type by reason of the expected very marked deformation of the  $O^{--}$  by the  $Me^{++}$  ion; or, the emission of the bands may be due to a form of the oxide molecule which may be written  $Me^+O^-$ . The band spectra of the halides of Zn, Cd, and Hg probably resemble those of the alkaline earth halides, but the less polar character of the compounds, especially those of Hg, favors the existence of  $MeX_2$  in addition to  $MeX$  bands.<sup>43</sup> Further study is being made of the points touched on above.

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halides. These bands appear to be rather similar to the CuX bands, except that the shift of the intensity maximum, in successive sequences on either side of the intense band-group which is presumably  $\Delta n = 0$ , away from the first head of the sequence, is here much more rapid. Assuming  $n' = 0$ ,  $n'' = 0$  for the most intense band, the bands for each compound can be expressed by quantum theory formulas of substantially the usual type:  $\nu = \nu^e + (a'n' - b'n'^2) - (a''n'' + b''n''^2)$ . Here  $\nu^e = A_1, A_2, B_1$ , or  $B_2$ , constituting an electronic multiplet. There is a major doublet separation  $B - A$ , which increases with the atomic weight of the metal and of the halogen and is of the same order of magnitude as that of the  $2p$  terms for the corresponding  $Me^+$  or M spectrum, and a minor doublet separation  $A_2 - A_1 = B_2 - B_1$ , which decreases with increasing atomic weight of the metal or halogen. It may be recalled that similar double doublets appear in the  $a$  bands of BO, the  $\gamma$  bands of NO, etc. The coefficients  $a'$  and  $a''$ , representing molecular vibration frequencies, are comparable with those of the Cu halides, and decrease, as might be expected, with increasing atomic weight of Me and of X. The positive sign of the coefficient of  $n'^2$  (which it seems impossible to avoid by any other reasonable assignment of vibrational quantum numbers) is not contrary to theory, although it differentiates these bands from all others hitherto analyzed.

<sup>46</sup> For further discussion of hydride bands, see R. S. Mulliken, Phys. Rev. **25**, 509, 1925. In CuH, and, as suggested to the writer by Dr. W. W. Watson, in MeH, it may be that the first valence electron is engaged in a non-polar bond with the H electron, while the second behaves as in CuX and MeX.

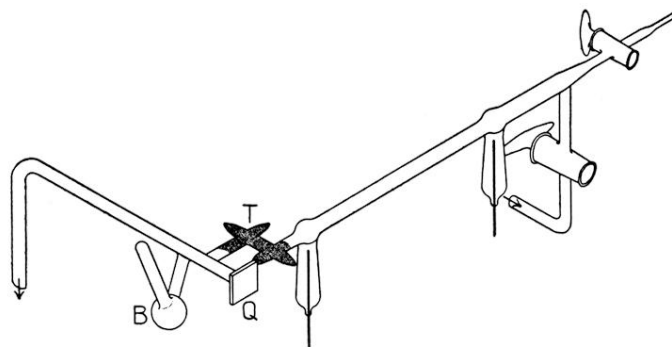


Fig. 1. Arrangement of discharge and afterglow tube for exciting spectra by means of active nitrogen.

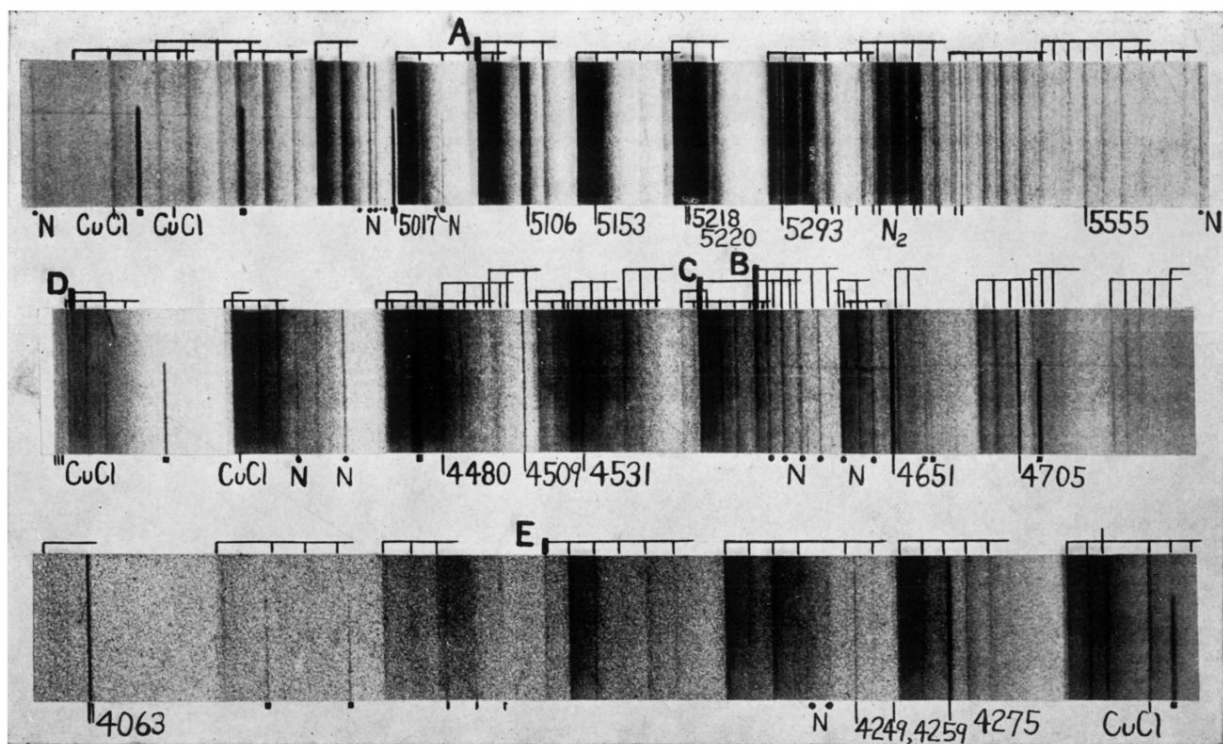


Plate I. Spectrograms showing most of the CuI bands.